EMANUEL LANDAU, Ph.D.
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POSITION HELD:

1. Coordinating Committee, Acid Rain Review, American Statistical Association, March 1984 to present; Staff Epidemiologist, American Public Health Association, July 1984 to present

2. Project Director, Environmental Health Hazard Project, American PUblic Health Association, January 1975 to June 1984.

3. Chief, Epidemiologic Studies Branch, Bureau of Radiological Health, DHEW, November 1971 to December 1974.

4. Epidemiologist, Office of the Assistant Administrator for Research and Monitoring, Environmental Protection Agency, 1971.

5. Epidemiologist, Office of the Assistant Administrator for Research and Development, Environmental Health Service, DHEW, 1969-1971.

6. Statistical Advisor, Office of the Associate Commissioner for Criteria and Standards Development, National Air Pollution Control Administration, 1965 to 1969.

7. Chief, Laboratory and Clinical Trials Section, National Cancer Institute, National Institutes of Health, 1962 to 1965

8. Chief, Biometry Section, Division of Air Pollution, PHS, 1959 to 1962.

9. California State Department of Public Health, 1957 to 1959. Assigned to the Air Pollution Medical Program, PHS, as a Supervisory Analytical Statistician.

EDUCATION:

1. Ph.D. American University, 1966 - (Evening Attendance)

2. B.A. College of the City of New York, 2/39 Graduate Work, CCNY, 2/39 - 6/39.

3. Enrolled for M.P.H. in School of Public Health at University of California, Berkeley, on part-time basis, did not complete due to reassignment to Washington, D.C.

PROFESSIONAL SOCIETIES:

> Royal Society Health (Fellow)
>
> American Public Health Association (Fellow)
>
> Biometric Society (ENAR)
>
> Population Association of America
>
> American Statistical Association
>
> Air Pollution Control Association
>
> Society of Occupational and Environmental Health (Councillor)
>
> Environmental Mutagen Society
>
> International Association of Survey Statisticians
>
> The Bioelectromagnetics Society
>
> Econometric Society
>
> American Economic Association

HONORS:

1. Superior Service Award (DHEW) April 11, 1963, on health effects of air pollution.

2. WHO Temporary Advisor on Air Quality Criteria, November-December, 1967.

3. Advisor on Air Quality Criteria, Karolinska Institute, Stockholm, Sweden, October 1968.

4. Advisor to Department of Transportation on biological effects of operating a fleet of supersonic planes, 1972-1974.

5. Consultant, Bureau of Radiological Health 1975-1983.

6. Consultant, EPA Environmental Criteria and Assessment, 1980-1981.

7. Chairman, Committee on Statistics and the Environment, American Statistical Association, 1984-1985.

8. Chairman, Committee on Biomedical Effects of Air Pollution, Air Pollution Control Association, 1972-1980, Member, Editorial Board, 1975-1983.

9. APHA representative to Steering Committee for Eighth Symposium on Statistics, Law, and the Environment October 1984.

10. Letter of Commendation, Senator Muskie 11/19/68.

11. Letter of Commendation, Commissioner, NAPCA 6/20/69.

12. Who's Who in the World, 1984-1985.

SITE VISITS:

1. Participated in Site Visits for AEC and ERDA.

2. Also participated in Site Visits for NIEHS.

Additional Consulting Services, 1985 to Present

1. General Motors Research Laboratories--review of epidemiologic and human laboratory studies of exposure to ozone including briefings of environmental staff at Warren, Michigan

2. Aerospace, Inc. and subsequently W/L Associates, Ltd., contractors to the Department of Energy--review of health effects of exposure to electromagnetic radiation including site visits

3. American University grant from Department of Justice--Role of pornography and Media violence in family violence, sexual abuse and exploitation and juvenile delinquency

4 . Enrionmental Protection Agency--review of epidemiologic studies of effects of particulate matter

5. Chairman, ASA/EPA research conference--Current assessment of combined toxicant effects

5. Evans, Lance S., Lewin, Keith F., Patti, Mitchell J., and Cunningham, Elizabeth A. (1983), "Productivity of Field-Grown Soybeans Exposed to Simulated Acidic Rain," *New Phytologist*, 93, 377–388.

6. Banwart, Wayne, letter dated October 14, 1983, with updated research summary (reference to research proposal 3).

7. Irving, Patricia, letter dated October 11, 1983, with updated plot plan (reference to research proposal 2).

8. Evans, Lance S., Dimitriadis, Leandros, and Hinkley, Deborah A. (1984), "Seed Protein Quantities of Field-Grown Soybeans Exposed to Simulated Acid Rain," *New Phytologist*, 97, 71–76.

9. Evans, Lanse S. (1984), "Detailed Description of Acid Deposition/Agriculture Project," unpublished report.

10. Banwart, Wayne L. (1984), "Detailed Description of Acid Deposition/Agriculture Project," unpublished report.

The key document for Project B is the research proposal "An Approach for Estimating Effects of Acid Deposition on Economically Important Agricultural Crops in the United States," by the Biomedical and Environmental Assessment Division, Brookhaven National Laboratory (Sept. 1983) and cover letter from Paul D. Moskowitz (Sept. 27, 1983). Additional materials are as follows:

1. Medeiros, Moskowitz, Coveney, and Thode, "Oxidants and Acid Precipitation: A Method for Identifying and Modeling Effects on United States Soybean Yield," paper presented at the 76th Annual Meeting of the Air Pollution Control Association, Atlanta, GA, June 19–24, 1983.

2. Medeiros, Moskowitz, Coveney, Thode, and Odem, "Oxidant and Acid Precipitation Effects on Soybean Yield: Cross-sectional Model Development," Manuscript submitted to *Environment International*.

3. Material from Neal Odem on autocorrelation and multicollinearity problems.

FORAST Review Report

EMANUEL LANDAU, BENEE F. SWINDEL, JAMES R. THOMPSON, and JOHN R. VAN RYZIN*

INTRODUCTION

The FORAST Review Team was formed, as one of several, by the American Statistical Association Coordinating Committee in consultation with EPA/ADAS (Robert Rosenthal) under a cooperative agreement between ASA and EPA for the review of statistical aspects of the EPA-sponsored research on the effects of acid deposition. The FORAST Review Team had responsibility for reviewing the project identified as Forest Responses to Anthropogenic Stress (FORAST), S. B. McLaughlin, Principal Investigator.

The team reviewed individually key documents relating critical aspects of the research, provided by the Principal Investigator (see Appendix).

The team then met at the Oak Ridge National Laboratories (ORNL) on April 25 and 26, 1984, to (a) hear further reports from research and sponsoring personnel, including S. B. McLaughlin, T. J. Blasing, T. W. Doyle, and V. A. Dale from ORNL and D. Bennett from EPA; (b) interact with research and sponsoring personnel on statistical problems, principles, and procedures for FORAST; and (c) develop the initial draft of this report. Invited observers included

Gary Oehlert, Princeton University, and Donald C. Peterson, Energy and Resource Consultants, Inc.

This report was reviewed by the ASA Coordinating Committee.

The illness of Robert Rosenthal, who had intended to put the FORAST work into context, prevented his participation in the evaluation.

PROJECT 2A REVIEW: REGIONALIZATION OF THE FOREST DECLINE STUDIES

Objective

The overall objective of this review was to address questions of inferences to a *regional* basis of forest decline statistics and presumed effects of acid precipitation on the yield of forests, as obtained from research projects funded primarily by EPA at ORNL and other institutions. The region to which the inference is to be directed is the Eastern United States.

More specifically, the review team was to do the following:

1. Review the statistical methods used in data analysis, estimation of acid deposition effects, and assessment of the precision of the estimated effects.

2. Review the usefulness and the limitations of each set of data to the *regional* inference of acid deposition effects on forest yield.

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certainty for regional estimates of forest decline and on the adequacy for this purpose of the data from studies being reviewed.

Review of Research

General Comments

The Committee agrees that the FORAST project does indeed represent a feasible prospective plan to quantify the temporal and spatial patterns of growth changes in dominant forests' trees at selected sites in the Eastern United States. We are less confident of the success of attempts to determine the influences of climate, competition, and soil properties on growth. The regional extrapolation of inferences from the small number of FORAST project sites in areas that have experienced recent decline is very difficult and seems very uncertain.

Specific Comments

The principal sources of response data are standard tree ring-increment cores from each of 15 trees (greater than 50 years old) for each of 6 or more species for each of 6 sites from each of 12 geographic locations. At each location, the 6 sites comprised 3 pairs; the two sites of each pair were selected on the basis of soil and site characteristics to test the hypothesis that they would differ in sensitivity to pollution effects. Because only a small portion (10%) of cores intercepted the tree pith, date of origin of the core, and hence current tree age, is ordinarily only approximately determined.

Since individual annual increments are used as the measure of each tree's response to ambient conditions each year, the investigators believed it extremely important to date precisely (beginning at the present and working backward as far as possible for each core) the exact year of occurrence of each annual increment. Sometimes extreme ring depression of abnormal growth (e.g., "false" rings occurring in midyear because of drought or defoliation) makes dating observed increments doubtful. Accordingly, cross dating (consisting of matching patterns in annual variations in increments from several cores) is being used to date more precisely individual annual increments. Only a small portion of sampled tree rings have been so cross dated. The review team failed to understand the importance of the exact date of the decline. It is possible that the sampling method employed may result not only in high variability but also in systematic bias in the results. Nevertheless, it is evident that the FORAST team is attempting to ensure precision in measuring and accuracy in dating each annual increment observable in approximately 14,000 increment cores comprising the primary response data.

Two fundamental problems are evident in the adopted sampling plan. The age of every sample tree increased one year every year throughout the years covered by the FORAST survey. The tree size, too, increased annually.

Overcoming biases due to sampling current older trees and younger trees from the past (which ultimately survived) could possibly benefit from a different sampling design—such as the periodic resurveys of a random sample of trees

as employed by the U.S. Forest Service. This is one reason for considering the Forest Service's data as a valuable source of independent information on possible tree growth decline.

It may be possible to reduce biases due to increasing tree size by abandoning the current, seemingly exclusive, emphasis on assessing response based on annual radial increment. Since annual basal area increments tend to be constant under uniform conditions [implying that radial increment declines with increasing tree size (*Southern Journal of Applied Forestry*, Nov. 1979) under uniform conditions], it is certainly thinkable that the annual basal area increment (easily derived from FORAST measurements) should be taken as the principal measure of response. At least this alternative deserves serious consideration by FORAST. In addition, FORAST data show that basal area increments are better correlated with various measures of competition between trees.

FORAST surveyors cored only dominant and codominant trees at least 50 years old. They are attempting to remove from the observed growth series effects of competition from trees near each sample tree. Various measures of such competition are under consideration, including direct measures of stand density (including stand basal area) and measures derived from them (e.g., stand biomass). Much experience tends to indicate that stand basal area is a good predictor of competition effects and is more easily and accurately measured (via prism counts) than alternative predictors. FORAST investigators tend to emphasize the derived predictor stand biomass. In the absence of evidence to the contrary, the review team suggests that measured stand basal area should be emphasized as the best available measure of current competition [T. C. Nelson and E. V. Brender (1962), *Forest Science*, 9, 8–14] and, further, that stand basal area in the recent past might be estimable by reversing the prism technique described by Fender and Brock [(1963) *Journal of Forestry*, 61, 109–133]. We are given to understand that such an investigation is contemplated.

Because aging trends and assumptions regarding optimum growth curves must be used in the analysis to determine the percentage of growth reduction due to different tree species, the results of the FORAST project must be viewed in the context of the apparently limited stand modeling being performed at ORNL.

The actual time series data using ring-width for the tree ring data, combined with the use of splines to smooth the series, appears to be a promising area of dendrology. It is appropriate that the personnel on the Oak Ridge FORAST project are applying these methods to document the growth of the stands of the 72 sites. The users should seriously question, however, the application of the spline functions whenever they yield other than common-sense results. We note, moreover, that the FORAST investigators may find it appropriate to seek in-house consultation about the full array of time series techniques currently available for their use.

The combination of the tree-ring series at different sites by averaging the series using a biweight mean needs to be further analyzed. The purpose of this average is to eliminate the effect of outlier trees that had a sudden growth spurt assumed to be due to changes in stand competition. The biweight mean, using a weighting of observations based on

should be encouraged to achieve the same result at the slight expense of a loss in theoretical efficiency. In any event, these are simply technical matters easily dealt with.

The adjustment of the averaged and smoothed ring-width series for climatic effects using the Palmer drought index by use of filtering techniques and regression equations is not clearly spelled out. The danger in such adjustments is that any systematic bias in the adjusted series will be attributed to pollution effects at a later stage of the analysis.

Compensation for aging trends in the ring-width series is particularly difficult. It seems that compensation needs to be done prior to the averaging of the raw ring-width data for each plot. If the data are averaged first, the individual data that would allow for the incorporation of tree aging in the data would be lost. If the trees within the plot were of roughly the same age, perhaps this would not be important. In any event, the use of optimum growth curves by the FORAST Project team to adjust for age effects for all 34 species is likely to contribute to the uncertainty present in the analysis. The experimental results presented do not suggest that the optimal growth curves can be used with much assurance as predictors of optimal growth. There is probably considerable variation in the adequacy of the growth curves that have been developed for different species. After these techniques have been applied, it is recommended that the data sets be tested for the influence of aging effects at each stand by such techniques as comparing the sample representing the younger half of the trees with the older trees.

It should be noted that the U.S. Forest Service has conducted periodic (10-year) inventories of American forests for a half-century. More than 150,000 relocatable plots are currently monitored nationwide within all forest types and land-ownership classes (public and private, industrial and nonindustrial). The initial objective was the compilation of a national timber inventory. However, the survey has consistently collected data (such as radial growth measurements) to provide needed information on timber growth and mortality. Current survey units have modern data processing facilities and are committed to supplying information in response to customized requests for it.

Clearly, this U.S. Forest Survey information is a valuable source of additional, nationwide, long-term, and statistically independent information on possible recent forest growth declines. The review team urges that FORAST and EPA not underestimate this resource as a potential mechanism for complementing, validating, and extending geographically any statistical inferences from FORAST. We wish to emphasize, however, that associations based on observational data alone cannot be used as the basis of causality inference.

The regional extrapolation of the data from the FORAST project sites is believed to be limited. Using the 72 points developed as sites in the FORAST program, the FORAST investigators will extrapolate over the Eastern United States. The output that the Principal Investigator described indicated the development of isopleth maps representing species decline over broad regions. This extrapolation seems very uncertain because of the many factors that may influence

from Forest Service sources, and EPA should explore how this could be accomplished. Furthermore, there would be much wisdom in planning sites more uniformly in the region. The present design is highly clustered, because of the initial character of the proposed research.

A related issue that has not been touched is the incorporation of still other research results within the FORAST project. The roles of climate stress and elevation stress, which are important segments of overall environmental stresses, need assessment.

In summary, the FORAST project will provide very well-described and rigorous data developed from 72 stands in the Eastern United States. Indeed, as J. W. Pratt said of the Neyman–Pearson formulation for testing statistical hypotheses, "it is so ingenious and so successful that it is liable to be credited with properties which it does not have and which its originators and developers have never claimed for it." It is not clear, for example, that the techniques being used to remove aging trends, competition, and climatic influences from the data are sufficient to provide an unambiguous time series of statistical residuals for testing the influence of atmospheric pollutants. They may be useful, however, for the purpose of relating the series. Furthermore, significant associations of the residuals with annual variation in atmospheric pollutants cannot be used to infer causality. Extrapolation of the FORAST data over the Eastern region must be questioned—the development of simple isopleths may be misleading.

PROJECT 2B REVIEW: ESTIMATION OF ACID DEPOSITION EFFECTS FROM FOREST DECLINE STATISTICS

Objective

The overall objective was a critical review of the use of cross-sectional analysis (multiple regression) on existing data bases (including forest damage statistics, pollution statistics, and meteorological data) to develop dose–response functions for acid deposition effects on forests.

General Comments

The FORAST project will provide an excellent data base for documenting growth decline at specific sites selected in the Eastern U.S. forests. We encourage, however, more specific site-by-site, species-by-species, very recent time analyses to try to gain a better understanding of growth characteristics as they relate to pollutant levels before placing much credence on the long-term models intended for use in estimating decline in the Eastern U.S. forests. We would also encourage modification of the highly clustered pattern of site locations. We would again caution that causality comments derived from regression analyses alone are not valid.

Specific Comments

It appears that quantifying growth characteristics on a site-by-site basis for each tree species and the associ-

and long term) is very worthwhile. The FORAST project should be able to make distinct contributions to this effort.

The use of the data and results of the site-by-site analyses to project to the entire Eastern U.S. forests is more problematic. Although this may be useful from the regulatory viewpoint, it should be cautioned that FORAST will not be able to do these projections with good reliability using the current data set.

The use of FORAST as input into the forest growth and succession model for East Tennessee (FORET) for stand simulation modeling is vague at this time, and it is hard to say how productive this might be. The use of FORET to examine various scenarios may be informative, but the FORET model should be regarded as analogous to a model of the economy—useful for speculation, not for prediction.

The problem of acid deposition appears complex. The mechanism and the components are unclear at this time. An attempt has been made to use historical series to establish relationships.

A specific objective of the FORAST project is to develop associations between the amount of calculated growth slow down and the air pollutant history. Since areal data on acid deposition and ozone concentration levels are not available prior to the mid-1970s, it was necessary to develop surrogate measures of pollution. This process contributes additional analytic uncertainties.

Regarding the long-term analyses, the main problem seems to be poor measurements of ozone and actual acid deposition data. The proposed combination of using the Palmer drought index and SO_2 and NO_2 emissions data to estimate acid deposition levels at each site on a yearly basis, which one can then correlate with the smoothed tree-ring series, appears worth doing. Because of the crudeness and imprecision of the acid deposition estimated series, however, it is not clear how reliable such analyses will be or what inferences are possible (especially on a regional or national level). The problem with ozone as a factor is even more limiting. The use of stagnation days as a surrogate is crude but may be the best available. Here again, any inferences or correlations will be difficult.

There seem to be many difficulties surrounding the use of historical air pollutant data and surrogates. The use of stagnation days to predict historical oxidant concentrations appears to be dependent on relationships between current oxidant concentrations and stagnation days. Because oxidant formation is very complex and a function of the availability of precursor concentrations that have changed significantly over time, reliance on stagnation days seems problematic. Relationships between NO_x concentrations and ozone concentrations may not provide much definition for the oxidant injury scale.

Even assuming that the adjustments for competition and climatic effects have been done appropriately, it appears that the FORAST project will have severe problems in attributing the adjusted growth decline to the various possible factors (acid rain, ozone, mineral deposition, etc.). It appears that adequate, accurate, and complete data at most of the U.S. National Atmospheric Deposition Program (NADP) network stations near the stands exist only since about 1975.

sition. As a result, we feel that additional attempts should be made to focus on any short-term trends in growth seen since 1975 and see, as accurately as possible, how these relate to ozone levels and deposition on a site-by-site basis. In addition to studying long-term historical trends in tree-ring series and how they relate to SO_2 and NO_2 emissions data, surrogates for ozone levels, and drought index data and their combinations to estimate acid deposition effects, should not a short-term study with better data also be done? Such short-term analyses will be guides to, and supportive of, more long-term analyses.

The FORET model, though useful as a research device that indicates forest stand succession and composition over time, may be inappropriately used if it is coupled with FORAST output to develop quantitative estimates of stand composition change. There are many functional forms and assumptions in the FORET model that may require further validation prior to its use as a predictor of quantitative changes in forest stand succession. A specific problem with the FORAST and FORET interface is that the FORAST project has growth estimates for approximately 30 species of trees, whereas the FORET model runs on approximately 70 species of trees in the Eastern U.S. On the other hand, errors in future stand growth rate and composition introduced by the prediction of the future rate of tree species growth can far exceed any FORET modeling errors.

Especially noteworthy is the enormous decline in sulfur dioxide emissions in the most polluting EPA regions. This, we believe, is relevant to the following question: Are the sources that produce acid rain on the decline, or are they increasing? The FORAST data should be examined to determine whether responses to sulfur deposition declines in the Northeastern U.S. are detectable.

The Committee also recommends temporal studies of local areas affected by sulfur dioxide pollutant, which reached a peak and then declined, as a key to understanding the recovery process of forests. The potential for such an investigation exists, using the Copper Hill, Cades Cove, Sudbury, and Trail data bases. A simple time series analysis using sulfur dioxide levels and growth records would be not only easy to carry out but also probably very revealing. There are clearly a number of such studies that could be conducted using data that need only be collated. If it should turn out that the present sulfur dioxide levels, for example, are below those at which Cades Cove began to recover, then that is surely useful and important information. This would give some guide concerning safe levels of pollutants and the temporal relations between pollutant levels and tree growth. However, the role of metals emitted by the smelter may confound the results.

In conclusion, we do *not* believe that the proposed regression study will produce reliable unbiased estimates of the dose effects on forests of acid deposition and ozone. Although the FORAST research is clearly of a high-quality scientific nature, it is of limited value for short-term decision making. Extreme caution must be used in inferring causality from the available data. We believe, however, that it may be possible to associate forest decline with the severity of air pollution.

APPENDIX: KEY RESOURCE MATERIALS

1. McLaughlin, S. B., Blasing, T. J., Mann, L. K., and Duvick, D. N. (1983), "Effects of Acid Rain and Gaseous Pollutants on Forest Productivity: A Regional Scale Approach," *APCA Journal*, 33, 1041–1049.

2. McLaughlin, S. B., West, D. C., and Blasing, T. J. (1984), "Measuring Effects of Air Pollution Stress on Forests Productivity: Perspectives, Problems, and Approaches," *TAPPI Journal*, 67, 74–80.

3. McLaughlin, S. B. (in press), "FORAST: A Regional Scale Study of Forest Responses to Air Pollutants," in *Proceedings of a Symposium on Pollution and the Productivity of the Forest* (Oct. 4–5), 1983, Washington, DC.

4. McLaughlin, S. B., Mann, L. K., Leal, C., Kornegay, F., and Blasing, T. J. (1985), "Acid Deposition: Empirical Source–Receptor Relationships," manuscript in preparation.

5. McLaughlin, S. B. (1984), "A Brief Outline of Project Objectives and Principal Data Analysis Procedures in the FORAST Project" (unpublished).

6. Phipps, R.L. (1983), "Procedure for Checking Reliability of Ring-Width Measurements of Collections Obtained for FORAST," January (unpublished).

7. McLaughlin, S. B., and Mann, L. K. (1983), "Interim Project Status Report for Forest Responses to Anthropogenic Stress (FORAST)," March (unpublished).

8. Doyle, Thomas W. (1983), "Competition and Growth Relationships in a Mixed-Aged, Mixed-Species Forest Community," unpublished Ph.D. dissertation, University of Tennessee, Knoxville.

Aquatic Research Review Report

G. P. PATIL, WALTER LIGGETT, FRED RAMSEY, and WOOLLCOTT K. SMITH*

1. INTRODUCTION

The Coordinating Committee on EPA–ASA peer review of statistical aspects of EPA-sponsored research on the effects of acid deposition formed the Aquatic Review Team in consultation with EPA/ADAS (Richard Barchet and John Malanchuk) under a cooperative agreement between ASA and EPA. As identified in earlier correspondence, the Aquatic Review Team had the responsibility of reviewing two documents pertaining to the following projects:

Project NSWS: National Surface Water Survey: National Lake Survey–Phase I Research Plan

Project ACID: Analysis of Trends in the Chemistry of Surface Waters of the United States Based on the Acidification Chemistry Information Database

The Aquatic Review Team reviewed the two documents from a statistical standpoint, met with concerned research investigators and sponsors July 23–25, 1984, and prepared this report.

The following EPA/ADAS scientists participated in the review meetings and discussions with John Malanchuk, coordinating the EPA participation: David Bennett, Ted Hinds, Tony Janetos, and John Malenchuk (all RD-676). The following research investigators of Project NSWS participated in the review meetings and discussions: Rick Linthurst, Kilkelly Associates, and Scott Overton, Oregon State University. The following Brookhaven National Laboratory investigators of Project ACID participated in the review meeting and discussions: George Hendrey, Chris Hoogendyk, Ed Kaplan, and Neal Oden.

This report was reviewed by the ASA Coordinating Committee.

2. PROJECT 3A: REVIEW OF NSWS DOCUMENT

Overall Conclusion. A primary goal of the NSWS National Lake Survey (NLS) is to obtain interval estimates of the number of lakes in defined geographic regions that may be sensitive to acid deposition. The proposed sampling design shows sizable effort behind it. Whether this is a most efficient design to achieve the multiple objectives needs to be examined in the light of alternative design options. The NSWS report assures that the survey is designed to meet concrete objectives. The objectives could be more specific and as stated, they do not state the error bounds desired. The design should be specifically linked with all of the important objectives—in particular, with the maintaining representative samples for Phases II and III.

2.1 Introduction

We divide our comments into two parts: general comments on the plan, followed by specific comments on the technical details or the lack of technical details in the plan. A short summary and recommendations follow.

A probability sample drawn from a fixed, well-defined sampling frame is a good general method for the primary goal of the survey, which is to estimate the percentage of susceptible lakes by region. With a well-defined sampling plan, standard results can be used

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PUBLICATIONS:

Albrecht, R. M. and Landau, E.: "Microwave Radiation: An Epidemiological Assessment." <u>Reviews on Environmental Health</u>, 3:43-58, 1979.

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Landau, E., Prindle, R.A., and Zeidberg, L.D.: "The Nashville Air Pollution Study. Sulfur Dioxide and Bronchial Asthma--A Multivariate Analysis." <u>Intern. J. Env. Studies</u>, 2:41-45, 1971.

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Schiffman, R. and Landau, E.: "Use of indexes of air pollution potential in mortality studies." J. APCA, 11:384-386, August 1961.

Speizer, F. and Landau, E.: "Epidemiologic studies of obstructive ventilatory diseases of the lung. II. A follow-back approach for studying mortality from obstructive ventilatory diseases of the lung." American Review of Respiratory Diseases, 83:826-841, June 1961.

Schoettlin, C. and Landau, E.: "Air pollution and asthmatic attacks in the Los Angeles Area." Public Health Reports, 76:545-548, June 1961.

Prindle, R. A. and Landau, E.: "The effect of air pollution on health in the United States." Vitalstoffe-Xivillsationskrankhelt Hoft 22 (V. 1. 2), 49-53, April 1961.

Landau, E. and Morton, J.C.: "An epidemiologic view of chronic pulmonary insufficiency in the United States." American Review of Respiratory Diseases, 83:3 and 4 pp. 405-407, March and April 1961.

Landau, E., Jones, F.V., and Schoettlin, C.E." "An air pollution map for the Los Angeles Basin," presented at the Second Air Pollution Research Planning Seminar, Cincinnati, Ohio, Feb. 3-7, 1958, pp. 166-170.

Landau, E.: "Design of a study for interpreting variations in respiratory disease mortality." The Second Air Pollution Research Conference, California State Department of Public Health, December 5-6, 1958, pp. 103-109.

Landau, E.: "Methods suitable for utilizing some existing data in air pollution research," presented at a Symposium on Statistical Methods in Air Pollution Research, The Fourth Air Pollution Medical Research Conference, California State Department of Public Health, December 7-9, 1960.

ADDENDUM TO SELECTED LIST OF PUBLICATIONS:

1. Based on work with <u>American Statistical Association</u>, Review report of an American Statistical Association Coordinating Committee FORAST Review Team to EPA National Acid Precipitation Assessment Program, April 1984 (attached).

2. Based on work with <u>American Public Health Association</u>, Landau E, Thompson DJ, Feldman RA, et al: Selected Non-Carcinogenic Effects of Industrial Exposure to Inorganic Arsenic. EPA 560/6-77-018, Washington, DC.

   Feldman RA., et al: Peripheral Neuropathy in Arsenic Smelter Workers, <u>Neurology</u> 29:939-944. July 1979.

   Landau E.: Neurological Effects of Long-Term Industrial Exposure to Inorganic Arsenic, 1978 Annual Meeting of APHA.

   Matanoski AM, Landau E, Tonascia J, et al: Lung Cancer Mortality in Proximity to a Pesticide Plant: An interim report. EPA 560/11-80-013, Washington, DC, 1980.

   Community Study of the Effects of Exposure to Fibrousglass Plant Emissions in Pennsylvania--A Resurvey, Report to EPA, Bahn A. and Landau E., 1978.

H. DANIEL ROTH

Roth Associates, Inc.
6115 Executive Boulevard
Rockville, Maryland 20852

Professional Background

1975 - present   President and founder, Roth Associates, Inc., Rockville, MD.

1973 - 1975   Senior ranking mathematical statistician, Environmental Protection Agency (EPA), Washington, D.C.; statistical consultant to the Assistant Administrator for Planning and Management.

1969 - 1973   Research and consulting, biomathematician-statistician, Information Systems Division, Smithsonian Institution, Washington, D.C.

1971 - 1988   Clinical assistant professor of Biostatistics, Georgetown University School of Dentistry, Georgetown, MD.

1971 - 1973   Statistical and information systems consultant to government and private agencies.

1967 - 1969   Instructor of theoretical mathematics, State University of New York at Stony Brook.

Academic Background

Ph.D.   Mathematics (Probability Theory) State University of New York at Stony Brook (1969)

M.A.   State University of New York at Stony Brook (1967)

M.A.   Hunter College, City University of New York Graduate Center (1965)

B.S.   Brooklyn College, City University of New York (1964)

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Summary of Professional Experience

I have experience in collecting and analyzing data, designing and carrying out surveys, developing mathematical and statistical models, and managing computer data bases. I have broad-based familiarity with data in the fields of: health and safety, medical drugs and devices, transportation, economics, the social sciences, as well as environmental pollution. My clients include: agencies of the United States and foreign governments; research institutions; trade associations; law firms; pharmaceutical, food, tobacco, and liquor companies; management consulting firms; automobile manufacturers; and metal, mining, machinery, construction, pesticide, and chemical companies. My work has been published in scientific journals and books, as well as technical reports, and has been presented at scientific meetings, university symposia, and federal government hearings.

AREAS OF EXPERTISE

My work includes projects in the following areas:

(1) Health and Safety

I have designed new studies and has analyzed data in the fields of: epidemiology, human clinical research, and animal toxicology. Specific projects have included evaluating the risks associated with: liquor consumption; occupational exposures to various chemicals in the workplace; water contaminants; electromagnetic fields; the use of new super absorbent baby diapers; the fallout of nuclear debris in the Marshall Islands; Salmonella poisoning in food products; passive smoking; the combined exposure to asbestos and smoking; gas cooking; and exposures to utility plant emissions and discharges. In the field of safety, I have examined the hazards of operating cranes and forklifts, performing various types of construction jobs in heavy industry, and working in railroad stockyards.

(2) Medical Drugs and Devices

I have designed clinical trials and has analyzed pharmaceutical data. For example, the firm has examined: the efficacy and safety of electrical devices designed to expedite the healing of bone fractures, artificial knees, and hip replacements; treatments to mitigate the effects of

chronic conditions such asthma; as well as drugs designed to suppress nausea during pregnancy.

(3) Transportation

A growing part of my research interests involve evaluating the risks, hazards, and economics of various aspects of transportation. Safety projects have included estimating the risks associated with: driving utility vehicles, passenger cars, and all terrain vehicles; using certain brand name tires; dismantling multiple and single rim wheels on trucks; and a spectrum of passenger car bumper designs. Economic studies conducted have included assessing: the costs of owning and operating different types of vehicles; the costs and benefits of different types of automobile bumpers; and practices for compensating vehicle owners for premature rusting, engine damage, or faulty tires.

(4) Social and Economic Issues

Among other projects in the social and economics area, I have analyzed: costs and trends of seafood consumption in Japan; changes in the U.S. Internal Revenue Code on the economy of Puerto Rico; methods for compensating for hurricane damage; the efficacy of the U.S. food stamp program in improving the nutritional intake of children; the cost and benefits of implementing pollution control devices; ramifications of fraudulent practices of selling vacuum cleaners; the economics of home kidney dialysis programs; and hiring practices in an equal opportunity industry. We also have conducted environmental audits and have performed cost-benefit analyses on the use of different types of industrial devices.

(5) Environmental

Activities in this area have involved designing new studies and assessing data bases maintained by others. Projects have included: analyzing species diversity and contamination patterns in waterways; examining outdoor air and water quality trends; analyzing occupational exposures to airborne pollutants; investigating the course of eroding shorelines; analyzing the fate of PCBs; and measuring electric and magnetic field exposures of individuals living within close proximity to transmission lines.

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(6)   Mathematics, Statistics, and Computer Programs

Designs include statistical and mathematical models as well as computer programs that are applicable to a broad range of problems. In the past I have worked on problems involving survey design, probability sampling, differential equations, and many data analytic techniques including multivariate analysis, survival analysis, and time series. In addition, my firm maintains large technical, as well as computer program libraries and has access to publications from the libraries at major universities in the Washington, D.C. area, the National Institutes of Health, the National Library of Medicine, and the National Bureau of Standards.

Publications, Scientific Articles, and Monographs

Freudenthal, P.C., Roth, H.D., Hammerstrom, T., Lichtenstein, C., and Wyzga, E., "Health Risks of Short-term SO_2 Exposure to Exercising Asthmatics," JAPCA 39:831-835, 1989.

Roth, H.D. and Post, E.S. "Evaluation, Analysis, and Technology Transfer of Safety and Evaluation Issues: Health Effects of Short and Long Term Exposure to Nitrogen Dioxide," Final Report Prepared for the Gas Research Institute, 1989.

Roth, H.D. and Post, E., "Assessment of the Cancer Epidemiology Data on Welders," Prepared for National Welding Defence, October 1989.

Roth, H.D. and Lichtenstein, C., "A Study of Activity Patterns Among a Group of Los Angeles Asthmatics," EPRI Research Project 940-5, November 1988.

Hammerstrom, T. and Roth, H.D., "Assessment of the Health Data on Cadmium," Prepared for Meridian Research Inc., November 1987.

Roth, H.D. and Post, E.S. "Analysis of the Consumer Product Safety Commission's Documents Entitled: Health Effects of Nitrogen Dioxide (July 1983)," "Nitrogen Dioxide Health Assessment, 1984," and Update on Health Effects Associated with Nitrogen Dioxide," Prepared for the Gas Research Institute, May, 1987.

Roth, H.D., "An Analysis of the Health Risks due to Vehicle Emissions of Manganese," Prepared for the Health Effects Institute, 1985.

H. Daniel Roth   Resume   Page 5

Roth, H.D., "An Evaluation of Published Studies Analyzing the Association of Carcinogenesis With Exposure to Magnetic Fields," Final Report, EPRI EA-3904, Project 1824-03, 1985.

Roth, H.D., Wyzga, R.E., Hayter, A.J., "Chapter 93: Methods and Problems in Estimating Health Risks from Particulates," Aerosols, Lewis Pub., pp. 837-857, 1984.

Roth, H.D. and Post, E.S. "Analysis of the Scientific Basis of EPA's Proposed National Ambient Air Quality Standards for Nitrogen Dioxide (23 February 1984)" Final Report Prepared for the Gas Research Institute, Project 84-0098, 1984.

Roth, H.D., Wyzga, R.E., and Hammerstrom, T., "The Use of Risk Assessment in Developing Health-Based Regulations," Statistics in the Environmental Sciences, ASTM STP 845, S.M. Gertz and M.D. London, Eds., American Society for Testing and Materials, pp. 46-65, 1984.

Roth, H.D. and Post, E.S. "NO_2 and Health Effects: Analysis of Selected Studies -- Phase II," Annual Report Prepared for the Gas Research Institute, Project 80-0112, 1983.

Roth, H. D. and Ripps, A., "Status of Health-Based Environmental Regulations". Edison Electric Institute, 1982.

Roth, H. D., "Chapter 3, Electric and Magnetic Fields: Summary of Developments," Electrical and Biological Effects of Transmission Lines: A Review, Bonneville Power Administration, U.S. Department of Energy, pp. 8-19, 1982.

Roth, H.D. and Post, E., "Controversy Over NO_2 and Health," J. of International Gas Research Institute, 1981.

Roth, H.D., "Data Quality and Analysis in Risk Assessment," Conference Proceedings". The Electric Power Research Institute Conference on Environmental Risk Assessment, 1981.

Roth, H.D., "Risk Assessment," Journal of the Air Pollution Control Association, Philadelphia, PA, 1981.

Roth, H.D., Viren, J.V., and Colucci, A.V., Evaluation of Community Health Environmental Surveillance Cystem (CHESS): New York Asthma Data 1971-72, Volume 1, Electric Power Research Institute, 1981.

Roth, H.D., and Viren, J. V., Evaluation of Community Health Environmental Surveillance System (CHESS): New York Chronic Respiratory Disease Data 1970-71, Electric Power Research Institute, 1980.

Roth, H.D., OSHA Beryllium Hearings: Analysis of Epidemiological Data, 1978.

Roth, H.D., Statistical Guidelines for Conducting a Rural Drinking Water Survey, EPA, 1977.

Roth, H.D., Viren, J.V., Colucci, A.V., Evaluation of Community Health Environmental Surveillance System (CHESS): New York Asthma Data 1970-71, Volume 1, Electric Power Research Institute, Publication number EA-450, 1977.

Roth, H.D., Viren, J.V., Colucci, A.V., Evaluation of CHESS: New York Asthma Data 1970-71, Volume 2, Electric Power Research Institute, Publication number EA-450, 1977.

Viren, J.V., Roth, H.D., Colucci, A.V., Asthma in Six Los Angeles Communities: An Outline of Findings Based on CHESS 1972-73, prepared for the Southern California Edison Company, 1977.

Roth, H.D., "First Report of the Environmental Measures Project: Analysis and Application of Environmental Indicators," Prepared for the EPA, 1975.

Roth, H.D., "Statistics Review Committee Report," Prepared for the EPA, 1974.

Roth, H.D., "Information Elements for Inclusion in the 1973 Revision of the Railroad Accident Form," Prepared for the Federal Railway Administration, 1973.

Roth, H.D. and Pierce, J., "Statistical Analysis of a Beach Environment Transport Problem," Smithsonian Contribution Series, 1973.

Buechner, H. and Roth, H.D., "Integrity of Lek Domains," American Zoologists, 1973.

Buechner, H. and Roth, H.D., "Territoriality in the Male Uganda Kob," American Zoologists, 1973.

Roth, H.D., "Ordination Techniques," Institute for Statistical Ecology Monograph, Pennsylvania State University Press, 1972.

Roth, H.D., "Cluster Analysis for the Environmental Sciences,"
    Smithsonian Institution Monograph, Smithsonian Press Vol. 11,
    No. 2, reprinted 1971 in Cuadernos de Historia Economica de
    Cataluna, 1972.

Roth, H.D. and Pierce, J., "Multivariate Statistical Analysis of
    Bioclastic Turbidites," International Journal for Mathematical
    Geology, 1972.

Roth, H.D. and Koritzer, R., "Statistical Advances in Dental
    Research," Journal Georgetown University Dental School, 1972.

Roth, H.D., and Olin, J., "Multifactor Analysis of Neutron
    Activation Data," 1972.

Roth, H.D. and Pierce, J., "Wave Refraction and Coastal
    Erosion," Journal Geological Society of America, 1970.

Roth, H. Daniel, "Limit Theorems for Dependent Random Variables,"
    Thesis, 1969.

Public Speaking Addresses and Seminars

"Comments on 'Direct Health Effects of Air Pollutants Associated
with Acidic Precursor Emissions (SOS/T-22)'." Presented at the
NAPAP International Conference, "Acidic Deposition: State of
Science and Technology," February 1990.

"Definition of Adverse Health Effects of Exercising Asthmatics
Exposure to Short-term SO_2." Presented at the 82nd Annual
Meeting of Air and Waste Management Association, June 1989.

"A Reanalysis of Recent Acid Aerosol Epidemiological Data."
Presented at the 82nd Annual Meeting of Air and Waste Management
Association, June 1989.

"An Activity Pattern Survey of Asthmatics." Presented at the
82nd Annual Meeting of Air and Waste Management Association, June
1989.

"An Activity Pattern Survey of Asthmatics." Presented at the
Conference on Human Activity Patterns, May 1988.

"Health Risks of Short-term SO_2 Exposure to Exercising
Asthmatics." Presented at APCA, June 1987.

"Risk Assessment for Criteria Air Pollutants." Presented at the meeting of the Society for Risk Analysis, November 1986.

"Design of Toxicologic Study by Epidemiology." Presented at Wayne State University's Conference, "Principles and Practice of Industrial Toxicology," June 1986.

"A Survey of Unvented Gas Heater Users." Presented at the American Society of Heating, Refrigerating and Air-Conditioning Engineers, Inc. (ASHRAE) Conference, April 1986.

"Evidence of the Association of Respiratory Symptoms and Heat Source in the NHANES II Survey." Presented at Air Pollution Control Association (APCA), June 1986.

"Generation of a Dose-Response Surface Describing Responses of Asthmatics to Short-term SO_2 Exposure." Presented at APCA, June 1985.

"Methods and Problems in Estimating Health Risks from Particulates." Presented at U.S.-Dutch International Symposium on Aerosols, May 1985.

Report on The Twenty-Third Hanford Life Sciences Symposium: "Interaction of Biological Systems with Static and ELF Electric and Magnetic Fields," 1985.

"The Use of Risk Assessment in Developing Health-Based Regulations." Presented at the Conference of American Society for Testing and Material, 1984.

"Can Industry Control and Regulate Environmental Health Hazards Itself?," Presented at the American Public Health Association, Washington, D.C., 1982.

"Risk Assessment," Presented at the Air Pollution Control Association, Philadelphia, PA, 1981.

"Risk Assessment," Electric Power Research Conference, New Orleans, Louisiana, 1980.

"Analysis of SO_2 Health Effects Data," Presented at the University of Texas, Austin, Texas, 1979.

"Statistical Pitfalls in Analyzing Occupational Health Data," Presented at the American Association for Industrial Health and the American Association for Occupational Medicine Conference, Williamsburgh, Virginia, September 1978.

"A Reanalysis of Prevalence Chronic Respiratory Disease Symptoms in Adults: A 1970 Survey of New York Communities," Presented at the Society of Industrial Mathematics Air Pollution Control Seminar, Stanford University Department of Statistics, 1978.

"Cluster Analysis and Medical Research Problems," Presented at the Department of Community Medicine, Ohio State Medical School, 1978.

"Health and Other Environmental Quality Indicators," Federal Statistics Users, Washington, D.C., 1975.

"Environmental Indicators," Ohio State University Symposium sponsored by the National Science Foundation, 1974.

"Spatial Distribution," American Anthropological Society annual meeting, Washington, D.C., 1974.

Advanced Statistics Seminar, Smithsonian Institution, 1973.

"Integrity of Lek Domains," American Association for the Advancement of Science Meetings, Washington, D.C., 1972

"Multivariate Methods in Ecology," Institute for Statistical Ecology Pennsylvania State University, sponsored by the NSF, USDA, and Ecology Association. Also chaired a week's session on multivariate modeling, 1972.

"Quantitative Research Methods," Georgetown University Medical Center, 1972.

Mathematics and Chemistry Seminar, Brookhaven National Laboratory, 1972.

"Multivariate Discriminant Analysis," Heidelberg University, West Germany, 1972.

"Mathematics in Scientific Research," Coppins State College, Baltimore, Maryland, 1972.

"Cluster Analysis," Sociology and Anthropology seminar, Smithsonian Institution, 1971.

"Quantitative Environmental Models," Smithsonian Institution, 1970.

"Analysis of Binary Data," Smithsonian Institution, 1969.

Professional Associations and Honors

Invited speaker NATO conference on Statistics and the Environment
-- University of Calgary (1974).

Superior Performance Award for research and consulting
Smithsonian Institution (1972).

Smithsonian Research Foundation Award for the development of
statistical models in health and environmental research
(1972).

National Science Foundation Award for the lectures on
multivariate statistical models in ecology at the Institute
for Statistical Ecology -- Pennsylvania State University
(1972).

Smithsonian Research Foundation Award for the development of
theoretical and applied models in sedimentology (1970-71).

Letters of commendation from the Secretary for the Smithsonian
for (1) upgrading the levels of mathematical and statistical
analysis and (2) conducting a series of biostatistical
seminars at the museum.

Referee several scholarly journals.

Panelist, the National Science Foundation (1972-74).

Member, the Bionetrics Society, the International Association of
Statistical Ecology, the American Association for the Advance-
ment of Science.

Fellowships, State University of New York at Stony Brook (1966-
69).

New York State Graduate Regents Scholar Awards (1965-68).

University Fellow, City University of New York (1964-65).

Mathematics Awards, City University of New York (1963-64).

CARL O. SCHULZ

EDUCATION

B.A., Chemistry, The College of Wooster, Wooster, Ohio, 1963

Ph.D., Organic Chemistry, The University of Cincinnati,
Cincinnati, Ohio, 1968

Postdoctoral Associate, Chemistry, Northwestern University,
Evanston, Illinois, 1968 - 1969

Postdoctoral Fellow, Environmental Medicine (Toxicology),
Johns Hopkins School of Hygiene and Public Health,
Baltimore, Maryland, 1971 - 1972

EMPLOYMENT

1983-Present	President, COSAR Inc., Consultants in Occupational and Environmental Toxicology
1985-Present	Adjunct Associate Professor of Environmental Health Sciences, University of South Carolina School of Public Health
1983-1985	Senior Toxicology Advisor, Clement Associates, Inc., Arlington, VA
1982-1983	Director, Division of Life Sciences, Clement Associates, Inc., Arlington, VA
1981-1982	Associate Director, Division of Life Sciences, Clement Associates, Inc., Washington, DC
1978-1982	Chief, Gastrointestinal and Contraceptive Drug Products Branch, Div. of OTC Drugs, Bureau of Drugs, U.S. Food and Drug Administration, Rockville, MD
1977-1978	Biological Program Specialist, Bureau of Veterinary Medicine, U.S. Food and Drug Administration, Rockville, MD
1976-1977	Petition Review Toxicologist, Bureau of Foods, U.S. Food and Drug Administration, Washington, DC

1974-1976   Senior Toxicologist, Center for Occupational
             Safety and Health, Stanford Research Institute,
             Arlington, VA

1972-1974   Research Associate, Dept. of Environmental
             Medicine, Johns Hopkins School of Hygiene and
             Public Health, Baltimore, MD

1969-1971   Research Chemist, Films-Packaging Division,
             Union Carbide Corp., Chicago, IL

PROFESSIONAL CERTIFICATION

     Diplomate of the American Board of Toxicology
          (recertified in 1989)

MEMBERSHIP IN PROFESSIONAL SOCIETIES

     Society of Toxicology
     Society for Risk Analysis
     Roundtable of Toxicology Consultants
     Carcinogenesis Specialty Section, SOT
     Risk Assessment Specialty Section, SOT
     American Association for the Advancement of Science
     New York Academy of Sciences
     Society of the Sigma Xi

OFFICES IN PROFESSIONAL SOCIETIES

     Chairman, Finance Committee, National Capital Area
          Chapter, SOT. 1983 - 1985.
     Secretary-Treasurer, Carcinogenesis Specialty Section,
          SOT, 1985 - 1988.
     Secretary-Treasurer, Southeastern Regional Chapter, SOT.
          1988 - present.

AREAS OF EXPERTISE

     Quantitative Risk Assessment
     Regulatory Toxicology
     Human Health Hazard Assessment
     Toxicology Study Design and Interpretation
     GLP Compliance and Data Auditing
     Chlorinated Dibenzodioxins (dioxin)
     Phenoxy Herbicides (Agent Orange, 2,4-D, 2,4,5-T)
     Formaldehyde
     Lead, Arsenic, Cadmium and Related Metals

PUBLICATIONS

Schulz, Carl O. 1989. Assessing human health risks from exposure to Di(2-ethylhexyl)phthalate (DEHP) and related phthalates: Scientific issues. Drug Metab. Rev. (In Press).

Lagoy, P.K., Nisbet, I.C.T., and Schulz, C.O. 1989. The endangerment assessment for the Smuggler Mountain site, Pitkin County, Colorado: A case study. In Paustenbach, D.J. (ed.). The Risk Assessment of Environmental and Human Health Hazards. J. Wiley & Sons, Inc., New York. Pp. 505-525.

Veterans Administration 1989. Synopsis of Scientific Literature on Phenoxy Herbicides and Associated Dioxins, No. 6 - (Volumes XIII and XIV). (C.O. Schulz, author)

Veterans Administration 1989. Review of the Literature on Herbicides, Including Phenoxy Herbicides and Associated Dioxins, Vol. XIII. Analysis of the Recent Literature on Health Effects, and Vol. XIV. Annotated Bibliography. (C.O. Schulz, prinicpal author)

Veterans Administration 1988. Synopsis of Scientific Literature on Phenoxy Herbicides and Associated Dioxins, No. 5 - (Volumes XI and XII). (C.O. Schulz, author)

Veterans Administration 1988. Review of the Literature on Herbicides, Including Phenoxy Herbicides and Associated Dioxins, Vol. XI. Analysis of the Recent Literature on Health Effects, and Vol. XII. Annotated Bibliography. (C.O. Schulz, prinicpal author)

Universities Associated for Research and Education in Pathology, Inc. (UAREP) 1988. Human Health Aspects of Environmental Exposure to Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans. Report of the Ad Hoc Panel on Health Aspects of Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans. UAREP, Inc., Rockville, MD.

Veterans Administration 1987. Review of the Literature on Herbicides, Including Phenoxy Herbicides and Associated Dioxins. Vol. IX. Analysis of Recent Literature on Health Effects and Vol. X. Annotated Bibliography. (C.O. Schulz, principal author)

Veterans Administration 1987. Synopsis of Scientific Literature on Phenoxy Herbicides and Associated Dioxins, No. 4 - (Volumes IX and X). (C.O. Schulz, author)

Schulz, C.O., LaGoy, P.K., and Paxton, M.B. 1986. Reviewing the literature on the health effects of phenoxy herbicides and associated dioxins. Chemosphere 15:2099

Veterans Administration 1986. Review of the Literature on Herbicides, Including Phenoxy Herbicides and Associated Dioxins. Vol. VII. Analysis of Recent Literature on Health Effects and Vol. VIII. Annotated Bibliography. (C.O. Schulz, principal author)

Veterans Administration 1986. Synopsis of Scientific Literature on Phenoxy Herbicides and Associated Dioxins, No. 3 - (Volumes VII and VIII). (C.O. Schulz, author)

Veterans Administration 1985. Review of Literature on Herbicides, Including Phenoxy Herbicides and Associated Dioxins. Vol. V. Analysis of Recent Literature on Health Effects and Vol. VI. Annotated Bibliography. (C.O. Schulz, principal author)

Veterans Administration 1985. Synopsis of Scientific Literature on Phenoxy Herbicides and Associated Dioxins, No. 2 - (Volumes V and VI). (C.O. Schulz, author)

Veterans Administration 1984. Review of Literature on Herbicides, Including Phenoxy Herbicides and Associated Dioxins. Vol. III. Analysis of Recent Literature on Health Effects and Vol. IV. Annotated Bibliography. (C.O. Schulz, Principal author)

Veterans Administration 1984. Synopsis of Scientific Literature on Phenoxy Herbicides and Associated Dioxins, No. 1 - (Volumes I - IV)

Taylor, J.M., Biskup, R.K. and Schulz, C.O. 1979. Good laboratory practices. FDA By-lines 9:187

Schulz, C.O. 1976. The xylene criteria document: A commentary. J. Occup. Med. 18:567

Schulz, C.O., Rubin, R.J. and Hutchins, G.M. 1975. Acute lung toxicity and sudden death in rats following the intravenous administration of the plasticizer, di(2-ethylhexyl)phthalate, solubilized with Tween surfactants. Toxicol. Appl. Pharmacol. 33:514

Rubin, R.J. and Schulz, C.O. 1975. Relation of the physical/chemical state of a plasticizer, bis(2-ethylhexyl)phthalate (DEHP) to its biological disposition and action. Proceedings of an International Symposium on Recent Advances in Assessing Health Effects of Environmental Pollutants, Vol. 2. Committee of European Communities, Paris, 1975. Pp. 903 - 912

Schulz, C.O. 1974. Acute lung injury from the interaction of a plasticizer, di(2-ethylhexyl)phthalate (DEHP) and a polysorbate surfactant, Tween 80. Fed. Proc. 33:224(abstract)

Schulz, C.O. and Rubin, R.J. 1973. Distribution, metabolism and excretion of di(2-ethylhexyl)phthalate in the rat. Environ. Health Perspect. 3:123

Kaplan, F., Schulz, C.O., Weisleder, D. and Klopfenstein, C.E. 1968. The geometry of myrtenal. A detailed analysis of the NMR spectrum of a bicyclo(3.1.1)hept-2-ene system. J. Organic Chem. 33:1728

Schulz, C.O. 1968. A Study of the Geometry and Chemistry of Myrtenal and Myrtenol. Ph.D. Dissertation, University of Cincinnati

Schulz, C.O. Stafford, F.E. 1968. The vapor phase infrared spectra of the niobium oxotrihalides, $NbOCl_3$, $NbOBr_3$, and $NbOI_3$. J. Phys. Chem. 72:4686

Kaplan, F. and Schulz, C.O. 1967. Long-range hydrogen-phosphorus spin-spin coupling in aromatic systems. Chem. Commun. 8:376

PRESENTATIONS

"Consumer Product Risk Assessment: Unique Problems in Estimating Population Exposures". The 1989 Washington Conference on Risk Assessment. Arlington, VA. September 26, 1989.

"An Update of the Review of Literature on the Health Effects of Phenoxy Herbicides and Associated Dioxins". Poster presentation at the 9th International Symposium on Chlorinated Dioxins and Related Compounds. Toronto, Ont., Canada. September 19, 1989.

"Human Risk Assessment from Exposure to Dioxins" A Public Forum entitled, What's Known About Dioxins, Paper Mills and Public Health? Georgetown, SC. June 22, 1989.

"The Role of the Toxicologist in Occupational Health". 12th Annual Educational Conference on Workers' Compensation. Hilton Head, SC. October 25, 1988.

"Current Approaches to Reducing Uncertainty in Risk Assessment". The 1988 Washington Conference on Risk Assessment, Arlington, VA. September 22 - 23, 1988.

"Risk Assessment". Epidemiology and Biostatistics Depart-
     mental Seminar. The University of South Carolina School
     of Public Health. Columbia, SC. March 3, 1988.

"Risk Assessments and Their Shortcomings". The Risk Manage-
     ment Subcommittee of the South Carolina Department of
     Health and Environmental Control Hazardous Waste Task
     Force. Columbia, SC. June 10, 1987.

"Toxicological Issues in the Development of an Occupational
     Health Standard for Formaldehyde". Spring meeting of the
     Carolinas Section of the American Industrial Hygiene
     Association. Winston-Salem, NC. April 10, 1987.

"Reporting the Results of a Risk Assessment". The 1986
     Washington Conference on Risk Assessment. Arlington, VA.
     October 28, 1986.

"What You Should Know About Performing a Risk Assessment". A
     series of one-day seminars on toxicological risk
     assessment sponsored by CEEM. Denver, CO. May 5, 1986.
     Chicago, IL. May 19, 1986. Boston, MA. June 2, 1986.

"Considerations in Assessing Risks at Hazardous Waste Sites"
     The 1985 Washington Conference on Environmental and
     Health Risk Assessment. Alexandria, VA. October 29,
     1985.

"Reviewing the Literature on the Health Effects of Phenoxy
     Herbicides and Associated Dioxins". Fifth International
     Symposium on Chlorinated Dioxins and Related Compounds.
     Bayreuth, Germany. September 17, 1985.

"Human and Environmental Effects of Mining Wastes".
     Remediation of Mining and Smelting Waste Sites Technical
     Information Transfer Workshop. Denver, CO. June 4,
     1985.

Symposium on the Impact and Direction of Good Laboratory
     Practices. Carl O. Schulz, Ph.D., Chairman. 96th Annual
     Meeting of the AOAC. Washington, DC. October, 1982

"Purposes for, and Impact of, GLP Regulations for Safety
     Testing". American Society for Microbiology Annual
     Meeting. Los Angeles, CA. May, 1979.

"Regulatory Toxicology: The Role of the FDA in Evaluating Test
     Data". Departmental Seminar, Dept. of Pharmacology and
     Toxicology, West Virginia University School of Medicine.
     Morgantown, WV. April, 1978.

"Long-term Values of the GLPs" 10th Annual Laboratory Animal
     Conference. Cincinnati, OH. April, 1978.

"Good Laboratory Practice Regulations and Their Impact on Feed Analysis". DRUSAFE West Spring Meeting, Chicago, IL. April, 1978.

"The Development of Good Laboratory Practices for Safety Testing". Sixth Food Microbiology Research Conference. Chicago, IL. November, 1977.

"Good Laboratory Practices and Drug Analysis". Fourth Annual Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies. Detroit, MI. November, 1977.

"The Development of Good Laboratory Practice Regulations for Nonclinical Laboratory Studies". Second Annual Seminar on Food Safety Regulations. Institute of Food Technologists, Laurel, MD. March, 1977.

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PAPERS

Lichtenstein, C.; Roth, H.D.; Walker, P.A.; Wyzga, R.E. (1989)
    An Activity Pattern Survey of Asthmatics. Presented at the
    82nd Annual Meeting of the Air & Waste Management Assoc.

Roth, H.D.; Walker, P.A. (1990) *An Analysis of Possible Health
    Effects Due to the Use of a Copper Diesel Fuel Additive.*
    Prepared for the Lubrizol Business Development Company.

ATTACHMENT A-2

Letter from Dr. Carl O. Schulz
to Dr. Neil Roth

COSAR Inc.

ATTACHMENT A-2

Consultants in Occupational and Environmental Toxicology

July 9, 1990

Neil Roth, Ph.D.
President
Roth Associates, Inc.
6115 Executive Blvd.
Rockville, MD 20852

Dear Neil:

I have reviewed the document entitled, "Potential Health Effects of Manganese in Emissions from Trap-Equipped Diesel Vehicles" prepared by the Health Effects Institute (HEI) in September 1988. Based on a review of the available literature on the human health effects of manganese at the time the authors of this report concluded that inhalation of airborne managanese contributed negligibly to daily exposures to this element and that the additional exposure that might be attributable to the use of manganese additives in diesel fuel would still result in inhalation exposures far below any that might be associated with adverse human health effects.

In order to assess the validity and objectivity of the HEI report, I have read several comprehensive reviews of the toxicology of manganese and its compounds that predated or are contemporaneous with the HEI document. These include the Environmental Health Criteria 17 for Manganese published by the World Health Organization in 1981, a review article by Cooper (1984), a chapter by John Donaldson from the NRC Canada report on Manganese in the Canadian Environment (1988) and a review article by Abbott (1987). I have also conducted a literature search and have reviewed information provided by Roth Associates, Inc. and have been unable to identify significant new scientific information that would:

> -indicate that exposure to manganese might lead to adverse health effects other than those indicated in the HEI report.
>
> -provide evidence that previously identified adverse human health effects occur at exposures below those indicated in studies reviewed in the HEI report.
>
> or
>
> -provide new information indicating that there are specific populations that are exceptionally sensitive to the known adverse effects of manganese.

The literature that has become available in the last few years consists primarily of review articles, commentaries, human case reports and epidemiologic studies. As will be seen in the overall review that comes from the current project, these documents tend to confirm what is already known about the toxicology of manganese and do not provide dramatic new information.

Those individuals who are concerned about the potential adverse health effects of chronic low-level exposure to airborne manganese base that concern on the absence of reports in the literature demonstrating the safety of such exposures rather than on any objective evidence that such exposures are harmful. They also speculate that a number of human neurologic disorders of unknown etiology but with symptomology resembling that of chronic manganese intoxication from high-level exposures may, in fact, be the result of environmental manganese exposures. These arguments tend to ignore evidence indicating that manganese intoxication is distinguishable from other neurologic disorders of unknown etiology and that the mechanism of manganese neurotoxicity has not been established.

While there is a some scientific uncertainty about both the no adverse effect level for human exposure to manganese by inhalation and the increase in airborne manganese concentrations that may result from the use of manganese in gasoline, the available evidence indicates that there is at least an order of magnitude difference between these two concentrations. The true "margin of safety" is probably much greater. In light of the evidence for homestatic mechanisms controlling the uptake and elimination of manganese and the absence of data indicating that manganese is a cumulative neurotoxin like lead, this margin of safety would appear to be adequate to protect the public health.

Sincerely yours,

Carl O. Schulz, Ph.D.,
DABT

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ATTACHMENT B-1

**United States Environmental Protection Agency,
Health Assessment Document for Manganese
(August 1984)**

United States
Environmental Protection
Agency

Environmental Criteria and
Assessment Office
Cincinnati OH 45268

EPA-600, 8-83-013F
August 1984
Final Report

Research and Development

PB 84-229954

⌒EPA

Health Assessment
Document for
Manganese

Final
Report
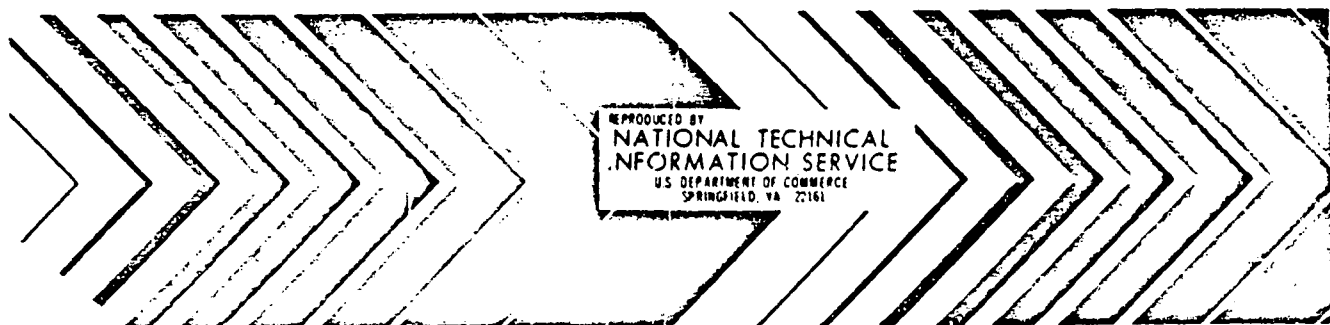
TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/8-83-01_?	2.	3. RECIPIENT'S ACCESSION NO. PB 84-229954
4. TITLE AND SUBTITLE Health Assessment Document for Manganese		5. REPORT DATE August 1984
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Erdreich, L.S. and Stara, J.F.		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Same as block 12		10. PROGRAM ELEMENT NO.
		11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS Environmental Criteria and Assessment Office Office of Research and Development U.S. Environmental Protection Agency Cincinnati, OH 45268		13. TYPE OF REPORT AND PERIOD COVERED FINAL
		14. SPONSORING AGENCY CODE EPA/600/22

15. SUPPLEMENTARY NOTES

16. ABSTRACT

This document evaluates data on occurrence, sources, and transport of manganese in the environment and data on metabolism, pharmacokinetics, laboratory toxicological and epidemiologic studies to determine the nature and dose response relationship of potential health effects on humans. Nationwide air sampling data indicate that mean manganese concentrations have declined from 0.11 $\mu g/m^3$ in 1953-1957 to 0.033 $\mu g/m^3$ in 1982. The effects of major concern to humans exposed to manganese are on neurological and on pulmonary function. The CNS effects have been observed in humans at exposure levels above 5 mg/m^3 and are incapacitating and generally irreversible. Data are equivocal between 1 and 5 mg/m^3 but suggest decreased prevalence. There are no reports of these effects below 0.3 mg/m^3 exposure. Pneumonia and chronic bronchitis occur at levels which are associated with neurological effects. Reduced lung function has been reported in children exposed to an estimated 3-11 $\mu g/m^3$ from emission of a ferromanganese plant. However, studies of workers exposed to 40 $\mu g/m^3$ did not show respiratory symptoms. Animal studies qualitatively support pulmonary effects of manganese exposure. Respiratory symptoms occur at lower levels than neurological symptoms and are therefore considered to be the critical effect based on available data.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT Public	19. SECURITY CLASS (This Report) Unclassified	21. NO. OF PAGES 353
	20. SECURITY CLASS (This page) Unclassified	22. PRICE

EPA Form 2220-1 (Rev. 4-77)   PREVIOUS EDITION IS OBSOLETE

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NOTICE

HEALTH ASSESSMENT
DOCUMENT FOR MANGANESE

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Research and Development
Office of Health and Environmental Assessment
Environmental Criteria and Assessment Office
Cincinnati, OH 45268

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NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

PREFACE

The Office of Health and Environmental Assessment of the Office of Research and Development has prepared this Health Assessment Document (HAD) at the request of the Office of Air Quality Planning and Standards (OAQPS). Manganese is one of several metals and associated compounds emitted to the ambient air which are currently being studied by the Environmental Protection Agency to determine whether they should be regulated as hazardous air pollutants under the Clean Air Act.

A Multimedia Health Assessment for Manganese had been drafted in 1979 to evaluate the health effects of manganese. The original document has since been modified in scope and emphasis and updated. This HAD is designed to be used by OAQPS for decision making.

In the development of this assessment document, the scientific literature has been inventoried, key studies have been evaluated and summaries and conclusions have been directed at qualitatively identifying the toxic effects of manganese. Observed effect levels and dose-response relationships are discussed where appropriate in order to identify the critical effect and to place adverse health responses in perspective with observed environmental levels.

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The EPA Office of Health and Environmental Assessment (OHEA) is responsible for the preparation of this health assessment document. The OHEA Environmental Criteria and Assessment Office (ECAO/Cin) had overall responsibility for coordination and direction of the document, preparation and production effort. Each chapter was originally drafted by the principal authors as listed below. The document managers are identified by an asterisk (*).

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1. INTRODUCTION

The purpose of this document is to summarize the current knowledge of the effects of exposure to environmental manganese upon human health. Manganese is an essential trace element for all living organisms, and chronic manganese toxicity from occupational exposure is well documented. For this reason, the potential human health hazard from environmental exposure must be evaluated. In order to assess the effects on human health, the general properties, ambient levels and biological availability of manganese from environmental media must be considered.

The rationale for structuring the document is based primarily on two major issues, exposure and response. The first portion of the document is devoted to manganese in the environment: physical and chemical properties, the monitoring of manganese in various media, natural and human-made sources, the transport and distribution of manganese within environmental media, and the levels of exposure. The second part is devoted to biological responses in laboratory animals and humans including metabolism, pharmaco-kinetics, mechanisms of toxicity, as well as toxicological effects of manganese.

This assessment document is based on original publications, although the overall knowledge covered by a number of reviews and reports was also considered. The references cited were selected to reflect the current state of knowledge on those issues which are most relevant for a health assessment of manganese in the environment.

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2. SUMMARY AND CONCLUSIONS

2.1. SUMMARY OF EXPOSURE

Manganese is a ubiquitous element in the earth's crust, in water and in particulate matter in the atmosphere. In the ground state, manganese is a gray-white metal resembling iron, but harder and more brittle. Manganese metal forms numerous alloys with iron, aluminum and other metals.

There are numerous valence states for manganese, with the divalent form giving the most stable salts and the tetravalent form giving the most stable oxide. The chlorides, nitrates and sulfates of manganese (II) are highly soluble in water, but the oxides, carbonates and hydroxides are only sparingly soluble. The divalent compounds are stable in acid solution, but are readily oxidized in alkaline conditions. The heptavalent form is found only in oxy-compounds.

Sampling of manganese in ambient air may be carried out by any of the methods used for collecting atmospheric particulate matter. High-volume samplers with glass fiber filters are widely used to measure total ambient aerosol. If information on particle size is desired the dichotomous sampler is often used, which separately collects fine (<2.5 μm) and coarse (> 2.5 μm) particles.

Water, soil and food are collected for manganese analysis by the usual techniques insuring representative sampling without contamination. Biological materials such as urine, blood, tissues, hair, etc., are collected and stored so as to prevent contamination by dust; no other special procedures are required when sampling for manganese analysis.

Sample preparation and analysis is the same for manganese as for other nonvolatile metals. Atomic absorption spectrophotometry, optical emission spectrometry and X-ray fluorescence are commonly used. Detection limits for manganese in air usually are as low as 0.002 μg/m^3.

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Very little manganese is mined in this country; some is mined domestic-
ally as low-grade ores, but most is imported. Ferromanganese and silico-
manganese are ferroalloys produced by the smelting of manganese ore in an
electric furnace. Manganese metal is produced by acid leaching of the ore,
precipitation of other metals, and electrolysis of the solution. Manganese
alloys and metal are then used to introduce manganese into steel or non-
ferrous alloys.

Metallurgy, especially steel making, accounts for ~95% of United
States demand for manganese. Production of manganese alloys is declining,
since demand has diminished recently and imports are increasing. The
remaining 5-6% of manganese demand is for a number of compounds which are
important in the chemical industry and in battery manufacture.

Methylcyclopentadienyl manganese tricarbonyl (MMT) has been produced and
used in small quantities as a fuel additive since 1958. Major use as an
octane improver in unleaded gasoline (at 0.125 g Mn/gal) began in 1974, but
was discontinued in 1978 due to adverse effects on hydrocarbon emissions.
MMT continues to be used at ~0.05 g Mn/gal in ~20% of leaded gasoline.

Manganese is the 12th most abundant element and fifth most abundant
metal in the earth's crust. While manganese does not exist free in nature,
it is a major constituent in at least 100 minerals and an accessory element
in more than 200 others. Its concentration in various crustal components
and soils ranges from near zero to 7000 µg/g; a mean soil content of 560
µg/g has been given. Crustal materials are an important source of atmo-
spheric manganese due to natural and anthropogenic activities (e.g., agri-
culture, transportation, earth-moving) which suspend dusts and soils. The
resulting aerosols consist primarily of coarse particles (>2.5 µm).

2-2

Manganese is also released to the atmosphere by manufacturing processes. Furnace emissions from manufacture of ferroalloys, iron, and steel are a major source of fine particulate emissions with a high manganese content. Fossil fuel combustion also results in manganese release. Coal fly ash is about equal to soil in manganese content, but contains particles finer in size. This is an important manganese source because of the volume of coal burned each year. Combustion of residual oil is less important because of its lower mangnese content. About 15-30% of manganese combusted in MMT-containing gasoline is emitted from the tailpipe.

The relative importance of emission sources influencing manganese concentration at a given monitoring location can be estimated by chemical mass balance studies. Studies in St. Louis and Denver suggest that crustal sources are more important in the coarse than in the fine aerosol fraction. Conversely, combustion sources such as refuse incineration and vehicle emissions predominantly affect the fine fraction. In an area of steel manufacturing, the influence of this process was seen in both the fine and coarse fractions.

Atmospheric manganese is present in several forms. Coarse dusts contain manganese as oxides, hydroxides or carbonates at low concentrations (≤ 1 mg Mn/g). Manganese from smelting or combustion processes is often present in fine particles with high concentrations of manganese as oxides (up to 250 mg/g). Organic manganese usually is not present in detectable concentrations.

Oxides of manganese are thought to undergo atmospheric reactions with sulfur dioxide or nitrogen dioxide to give the divalent sulfate or nitrate salts. Manganous sulfate has been shown to catalyze SO_2 transformation to sulfuric acid, but the manganese concentration necessary for a significant catalytic effect has been disputed.

2-3

Atmosp ric manganese is transported by air currents until dry or wet deposition occurs. In New York City, dry deposition occurred more quickly for manganese than most other metals, because it tended to be present in larger particles. Dry deposition of manganese averaged 300-670 ng/cm^2/ month, whereas wet deposition was ~120 ng/cm^2/month. Over much of the United States in 1966-1967, wet deposition of manganese ranged from <10-540 ng/cm^2/month. Near a ferromanganese plant in 1964-1965, dry deposition was as high as 19,300 ng/cm^2/month.

In water or soil, manganese is usually present as the divalent or tetra-valent form. Divalent manganese is soluble and relatively stable in neutral or acidic conditions. Manganese tends to be mobile in oxygen-poor soils and in the groundwater environment. Upon entering surface water, manganese is oxidized and precipitated, primarily by bacterial action If the sediments are transported to a reducing environment such as lake bottom, however, microbial reduction can occur, causing re-release of divalent manganese the water column. Manganese is bioconcentrated (by a factor of 10^3-10^4) in lower organisms; however, the concentration factor decreases (10-10^2) as trophic level increases. Thus biomagnification of manganese does not occur.

A rough assessment of trends in nationwide air sampling data indicates that manganese concentrations have declined during the period of record. The arithmetic mean manganese concentration of urban air samples decreased from 0.11 $\mu g/m^3$ in 1953-1957 to 0.073 $\mu g/m^3$ in 1966-1967, and to 0.033 $\mu g/m^3$ in 1982. In 1953-1957, the percentage of urban stations with an annual average of >0.3 $\mu g/m^3$ was ~10%. By 1969 these had dropped to <4%, and since 1972 the number has been <1%.

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The highest manganese concentrations, with some observations exceeding 10 $\mu g/m^3$, were seen in th. 1960s in areas of ferromanganese manufacture. More recent measurements in these areas indicated decreases of at least an order of magnitude had occurred, although definitive studies were not available.

Manganese is associated with both fine (<2.5 μm) and coarse (>2.5 μm) particles, but the manganese concentration in each fraction is highly variable. On the average, $\leq$16% of manganese in aerosol mass is found in fine particles; however, it is estimated that in some situations the fine fraction could contain as much as 50%.

Manganese concentrations in nonpolluted freshwaters are usually <20 $\mu g/\ell$, but ma/ exceed 1000 $\mu g/\ell$ where polluted. Concentrations in groundwater typically are higher than in surface water. Concentrations $\geq$1000 $\mu g/\ell$ are found in some drinking waters, but ~95% of water supplies contain man(anese at <100 $\mu g/\ell$. A median concentration of 4 $\mu g/\ell$ for public supplies has been reported.

Total human exposure to manganese may be estimated from information on levels in air, water and diet. Inhaled particles can be deposited either extrathoracically, in the tracheobronchial region, or in the alveoli. Time required for particle clearance and probability of absorption increases with increasing depth of deposition in the respiratory tract. Deposition of manganese in the alveoli can be calculated from the ambient concentration and the fraction present in fine particles. Thoracic (tracheobronchial plus alveolar) deposition is calculated from estimates of the manganese found in particles $\leq$15 μm in size. Alveolar deposition of manganese at current ambient levels is estimated as 0.072 $\mu g/day$ as an average and 6.6 $\mu g/day$ under high exposure conditions. Estimates of total thoracic deposition are

slightly higher; 0.26 µg/day (average) and 10.0 µg/day (high). Alveolar and total thoracic deposition under the high exposure conditions (10 µg/m^3) noted at certain locations in the 1960s were estimated to be 100 and 152 µg/day, respectively.

Diet is the main source of ingested manganese. Average adult intake has been variously estimated at 2.3-5.5 mg/day. On a body-weight basis, exposure increases from 0.002-0.004 mg/kg/day in infants to 0.06-0.08 mg/kg/day in adults. Drinking water usually comprises only a very small proportion of total ingestion exposure. The median intake level via drinking water is ~0.008 mg/day, but can be as high as ~2.0 mg/day for some water supplies. The ingestion of particles cleared from the respiratory tract is an even smaller source, probably constituting no more than 0.01 mg/day under the highest ambient exposure conditions currently observed.

2.2. SUMMARY OF BIOLOGICAL ROLE AND HEALTH EFFECTS

2.2.1. Biological Role.

Manganese is widely distributed within the human and animal body in constant concentrations which are characteristic for individual tissues and almost independent of the species. The highest values of manganese in humans are found in liver, kidney and endocrine glands. Manganese has been shown to penetrate the blood-brain and placental barriers. Animal data indicate a higher manganese accumulation in suckling animals, especially in the brain.

Manganese elimination from the body is accomplished mainly via feces. Biliary excretion is predominant under normal conditions although excretion via the pancreas and intestinal wall are considered to be important in conditions of biliary obstruction or manganese overload. In humans and in animals urinary excretion is low. The total body clearance of manganese in humans can be described by a curve which is the sum of at least two exponen-

tial functions with half-times of 4 and 40 days, respectively. However, the physiological significance of the estimated half-times cannot be obtained from this data.

Manganese metabolism is rigorously controlled by homeostatic mechanisms. The homeostatic control is primarily exerted at the level of excretion; however, the site of gastrointestinal (GI) absorption may also be an impor. control point. The absorption, retention and excretion of manganese e interrelated and respond very efficiently to an increase in manganese concentration. The GI absorption depends not only on the amount ingested and tissue levels of manganese, but also on manganese bioavailability and interaction with other metals. The influence of tissue concentrations on the excretory mechanism is still unknown.

It is generally accepted that under normal conditions 3-4% of orally ingested manganese is absorbed in man and other mammalian species. Gastrointestinal absorption of manganese and iron may be competitive. This interaction has a limited relevance to human risk assessment under normal conditions. However, it does lead to the hypothesis that iron-deficient individuals may be more sensitive to manganese than the normal individual.

2.2.2.   Toxicity. The acute toxicity of manganese is greater for soluble compounds and via the parenteral route. Acute poisoning by manganese in humans is very rare. Along with a number of other metals, freshly formed manganese oxide fumes have been reported to cause metal fume fever.

The major systems affected by chronic exposure to manganese in humans are the CNS and pulmonary systems. The neurological disorder known as chronic manganese poisoning, or manganism, resulting from occupational exposures to manganese dusts and fumes is well documented. Earlier studies report advanced cases of manganism in various miners, but more recent

studies report cases showing neurological symptoms and signs at much lower exposure concentrations.

These reports include no longitudinal studies and are therefore not adequate to identify a dose-response relationship, but do permit the identification of the lowest-observed-effect level (LOEL). The full clinical picture of chronic manganese poisoning is reported less frequently at exposure levels below 5 mg/m^3. The reports of a few early signs of manganism in workers exposed to 0.3-5 mg/m^3 suggest 0.3 mg/m^3 (300 $\mu g/m^3$) as a LOEL. The data avai'ble for identifying effect levels below 0.3 mg/m^3 is equivocal or in...equate. This is further complicated by the fact that good biological indicators of manganese exposure are not presently available. Also, there are neither human nor animal data suggesting the rate of absorption of manganese through the lung; therefore, extrapolating from other routes of exposure would be difficult.

Only one animal study utilized inhalation exposure to study neurotoxicity, resulting in no exposure-related effects on electromyograms or limb tremor effects in monkeys after 3 months exposure to 11.6, 112.5 and 1152 $\mu g/m^3$ Mn_3O_4.

Chronic treatment of rats with $MnCl_2$ in the drinking water throughout development is associated with selective regional alteration of synaptosomal dopamine uptake but not of serotonin or noradrenaline uptake. The brain regional manganese concentrations show dose-dependent increases and in treated animals, the changes in synaptosomal dopamine uptake is associated with decreased behavioral responses to amphetamine challenge. These observations are consistent with the hypothesis that in chronic manganese toxicity the central dopaminergic system is disturbed, providing a mechanistic explanation for the extrapyramidal disturbances seen in human manganism.

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The toxic effects of manganese on the pulmonary system vary in type and severity. There are several reports of humans developing pneumonia after occupational exposures to manganese at levels higher than the present TLV of 5 mg Mn/m^3. Chronic bronchitis has been reported to be more prevalent in workers exposed to 0.4-16 mg/m^3, but below 0.04 mg/m^3 (40 $\mu g/m^3$) respiratory symptoms were not increased over controls. However, conclusions about these exposure/response relationships are limited by the broad range of exposure values. Also, the health effects of simultaneous exposures to other toxic substances, such as silica, have also not been thoroughly examined.

One study in schoolchildren supported an association between increased respiratory symptoms and exposure to the manganese dusts emitted from a ferromanganese plant at levels estimated to correspond to 3-11 $\mu g/m^3$. The study involved several hundred children, had a participation rate of over 97% and documented monitored levels for settled manganese dust for several years. It is plausible that exposure to manganese may increase susceptibility to pulmonary disease by disturbing the normal mechanism of lung clearance.

Inhalation studies of pulmonary effects in animals show the occurrence of acute respiratory effects when the level of exposure exceeds 20 mg/m^3 of MnO_2. Mice and monkeys exposed to MnO_2 via inhalation showed pathological effects at 0.7 mg/m^3 after 14 days of exposure. This represents the lowest level at which adverse effects were observed after inhalation exposure to MnO_2. There is little data on toxicity after chronic exposure to MnO_2 levels between 0.1 and 0.7 mg/m^3. Several studies do exist where animals were exposed to ~0.1 mg/m^3 MnO as Mn_3O_4 particle or aerosols of respirable particle size, an appropriate form for health risk

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evaluation for airborne manganese. These studies have a variety of defi-
ciencies such as lack of description of pathological examination, small
study size and short exposure period. The clustering of negative results
around this level suggests that major adverse effects such as gross patho-
logical changes are absent.

Reports of impotence in a majority of patients with chronic manganese
poisoning are common, however, no other supporting human data are available.
Existing animal data addressing reproductive failure in males describe
long-term dietary exposure to manganese. Results show that dietary levels
up to 1004 ppm as $MnSO_4 \cdot 7H_2O$ and up to 3550 ppm as Mn_3O_4 were
almost without effect on reproductive performance. However, these and other
observations need to be verified using well-defined reproductive testing
protocols.

Although other effects of exposure to manganese have been reported in
animals, none have been observed consistently. In some cases the implica-
tions for human health are uncertain.

There is some evidence of carcinogenic activity of manganese in labora-
tory animals in the literature, although problems exist with regard to the
value of these studies (i.e., local injection site sarcomas in F344 rats, a
marginal response in Strain A mice, and inadequate data in the experiment
with DBA/1 mice). There is no epidemiologic information relating manganese
exposure to cancer occurrence in humans.

Divalent manganese ion has elicited mutagenic effects in a wide variety
of microbial systems, probably by substitution for magnesium ion and inter-
ference with DNA transcription. Attempts to demonstrate mutagenic effects
of manganese in mammalian systems have failed to show significant activity.
Two recent studies suggest that excess manganese during pregnancy affects

behavioral parameters, but there is insufficient evidence to define manganese as teratogenic.

2.3. CONCLUSIONS

The effects of major concern to humans exposed to manganese are chronic manganese poisoning and a range of pulmonary effects. The effects on the CNS are incapacitating and generally irreversible in its fully developed form, and have been reported at manganese exposure levels above 5 mg/m^3. There have been no reports of CNS effects below 0.3 mg/m^3 exposure. Data is equivocal between 1 and 5 mg/m^3 but suggest decreased prevalence. Studies below 1 mg/m^3 report some signs of the disease. There is little supportive animal data.

The pulmonary effects include pneumonia and chronic bronchitis at levels which are also associated with neurological effects. An increased prevalence of temporary respiratory symptoms and lower mean values on objective tests of lung function were reported in children exposed to an estimated 3-11 $\mu g/m^3$ from emissions of a ferromanganese plant. In comparison, studies of a smaller number of workers exposed to <40 $\mu g/m^3$ resulted in the conclusion that symptoms were generally unrelated to exposure to manganese. There are no data describing the effects of manganese exposure in asthmatics or other sensitive individuals.

Animal studies report increased susceptiblity to infection and radiological changes in the lungs associated with manganese exposure, thus qualitatively supporting the respiratory affect as the endpoint of concern. Respiratory symptoms occurred at lower levels than neurological symptoms and are therefore considered to be the critical effect.

The available evidence for manganese carcinogenicity in humans would be rated Group 3 overall using the International Agency for Research on Cancer

(IARC) criteria, because of inadequate data in animals and lack of any available data in humans. Clearly, more information is needed before a more definitive conclusion can be made about the carcinogenicity of manganese and its compounds.

3. GENERAL PROPERTIES AND BACKGROUND INFORMATION

3.1. PHYSICAL AND CHEMICAL PROPERTIES

Manganese is a ubiquitous element in the earth's crust, in water, and in particulate matter in the atmosphere. Manganese was recognized as a new element by C.W. Scheele, Bergman and others, but it was first isolated by J.G. Gahn in 1774 on reducing the dioxide with carbon. Some ores have been known and used since antiquity, e.g., pyrolusite (MnO_2) in glass bleaching (Weast, 1980; Reidies, 1981).

Manganese (Mn) is a steel gray, lustrous, hard brittle metal, too brittle to be used unalloyed. It exists in four allotropic forms of which the α-form is stable below $710^\circ C$. Manganese has only one stable natural isotope, ^{55}Mn. The manganese atom in the ground state has the electronic configuration $(1s^2)$ $(2s^2)$ $(2p^6)$ $(3s^2)$ $(3p^6)$ $(3d^5)$ $(4s^2)$ and six possible orientations of the 5/2 nuclear spin (Matricardi and Downing, 1981). Some physical properties of manganese are listed in Table 3-1.

Manganese exists in 11 oxidation states from -3 to +7, including 0, since the outer electron levels, $3d^5 4s^2$, can donate up to seven electrons. The compounds most environmentally and economically important are those containing Mn^{2+}, Mn^{4+} and Mn^{7+}. The Mn^{4+} is significant because of the important oxide, MnO_2. The +2 compounds are stable in acid solution but are readily oxidized in alkaline medium. The +7 valence is found only in oxy-compounds (Reidies, 1981). Normal oxidation potentials of manganese couples are given in Table 3-2.

TABLE 3-1

Physical Properties of Manganese*

Property	Value
Atomic number	25
Atomic weight	54.9380
Density	7.43 at 20°C
Melting point	1244°C
Boiling point	1962°C
Specific heat	0.115 cal/g at 25.2°C
Moh's hardness	5.0
Solubility	Soluble in dilute acids; reacts slowly in hot or cold water.

*Source: Weast, 1980; Matricardi and Downing, 1981; Reidies, 1981

TABLE 3-2

Normal Oxidation Potentials of Manganese Couples[a]

Oxidation State	Reaction	E°
	Acid Solution	
0, +2	$Mn \rightleftharpoons Mn^{2+} + 2e$	+1.18
+2, +3	$Mn^{2+} \rightleftharpoons Mn^{3+} + e$	-1.51
+2, +4	$Mn^{2+} + 2H_2O \rightleftharpoons MnO_2(py)^{[b]} + 4H^+ + 2e$	-1.23
+2, +7	$Mn^{2+} + 4H_2O \rightleftharpoons (MnO_4)^- + 8H^+ + 5e$	.51
+4, +6	$MnO_2 + 2H_2O \rightleftharpoons (MnO_4)^{2-} + 4H^+ + 2e$	-2.26
+4, +7	$MnO_2(py)^{[b]} + 2H_2O \rightleftharpoons (MnO_4)^- + 4H^+ + 3e$	-1.695
+6, +7	$(MnO_4)^{2-} \rightleftharpoons (MnO_4)^- + e$	-0.564
	Basic Solution	
0, +2	$Mn + 2(OH)^- \rightleftharpoons Mn(OH)_2 + 2e$	+1.55
+2, +3	$Mn(OH)_2 + (OH)^- \rightleftharpoons Mn(OH)_3 + e$	-0.1
+2, +4	$Mn(OH)_2 + 2(OH)^- \rightleftharpoons MnO_2(py)^{[b]} + 2H_2O + 2e$	+0.05
+4, +6	$MnO_2 + 4(OH)^- \rightleftharpoons (MnO_4)^{2-} + 2H_2O + 2e$	-0.60
+4, +7	$MnO_2(py)^{[b]} + 4(OH)^- \rightleftharpoons (MnO_4)^- + 2H_2O + 3e$	-0.588
+6, +7	$(MnO_4)^{2-} \rightleftharpoons (MnO_4)^- + e$	-0.564

[a]Source: Hay, 1967

[b](py) indicates pyrolusite made from decomposition of $Mn(NO_3)_2$ on which consistent values can be obtained.

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3.1.1. Manganese Compounds. Manganese forms numerous alloys with iron (ferromanganese, silicomanganese, Hadfield manganese steel) and with other metals like aluminum alloys, aluminum-bronzes, constantan, manganese-bronze, Monel, nickel-silver, and nickel-chromium resistance alloys. Several important compounds of manganese are described below and in Table 3-3.

3.1.1.1. MANGANESE (I) COMPOUNDS --

3.1.1.1.1. Methylcyclopentadienyl Manganese Tricarbonyl (MMT) -- $CH_3C_5H_4Mn(CO)_3$ or MMT is a light amber liquid added to fuels as an antiknock agent or smoke suppressant. It is formed by reaction of methyl-cyclopentadiene with manganese carbonyl [$Mn_2(CO)_{10}$].

3.1.1.2. MANGANESE (II) COMPOUNDS --

3.1.1.2.1. Manganous Carbonate -- $MnCO_3$ occurs naturally, but the commercial product is made by precipitation from manganese sulfate solutions. It is used in ferrite production, animal feeds, ceramics, and as a source of acid soluble manganese.

3.1.1.2.2. Manganous Chloride -- $MnCl_2$ exists in anhydrous form and as hydrate with 6, 4, or 2 water molecules. It is used as a starting material for other manganese compounds and in anhydrous form as a flux in magnesium metallurgy.

3.1.1.2.3. Manganese Ethylenebisdithiocarbamate -- $(CH_2NHCS_2)_2Mn$ is a yellow powder used under the name of "Maneb" as a fungicide. It is produced by treating a solution of manganous chloride containing sodium hydroxide and ethylenediamine with carbon disulfide and neutralizing the resulting solution with acetic acid.

3.1.1.2.4. Manganous Acetate -- $Mn(C_2H_3O_2)_2 \cdot 4H_2O$ is in the form of pale red, transparent crystals. It is soluble in water and alcohol. It is used as a mordant in dyeing and as a drier for paints and varnishes.

TABLE 3-3

Physical Properties of Some Manganese Compounds*

Name and CAS Registry Number	Valence	Chemical Formula	Molecular Weight	Specific Gravity	Melting Point, °C	Boiling Point, °C	Solubility
Methylcyclopentadienyl manganese tricarbonyl (MMT) [12108-13-3]	+1	$CH_3C_5H_4Mn(CO)_3$	218.09	1.39(20°)	1.5	233	Insoluble in H_2O. Soluble in most organic solvents
Manganous oxide [1344-43-0]	+2	MnO	70.94	5.37(23°)	1945		Insoluble in H_2O.
Manganous carbonate [598-62-9]	+2	$MnCO_3$	114.94	3.125	Decomposes		65 mg/ℓ (25°C) Soluble in dilute acid. Insoluble in NH_3 and alcohol.
Manganous chloride [7773-01-5]	+2	$MnCl_2$	125.84	2.997 (25°)	650	1190	622 g/ℓ (10°C) 1238 g/ℓ (100°C) Soluble in alcohol. Insoluble in ether and NH_3.
Manganous acetate [15243-27-3]	+2	$Mn(C_2H_3O_2)_2 \cdot 4H_2O$	245.08	1.589			Soluble in cold H_2O and alcohol.
Manganous sulfate [7785-87-7]	+2	$MnSO_4 \cdot H_2O$	169.01	3.25	Decomposes 850		Soluble in one part cold and 0.6 part boiling water; insoluble in alcohol.
Trimanganese tetraoxide [1317-35-7]	+2, +3	Mn_3O_4	228.81	4.84	1560		Insoluble in H_2O.
Manganese dioxide [1313-13-9]	+4	MnO_2	86.94	5.026	Decomposes 500-600		Insoluble in hot or cold H_2O, HNO_3, or acetone. Soluble in HCl.
Potassium permanganate [7722-54-7]	+7	$KMnO_4$	158.04	2.703 (20°)	Decomposes 200-300		28.3 g/ℓ (0°C) 250 g/ℓ (65°C) Decomposes in alcohol. Soluble in H_2SO_4. Very soluble in methyl alcohol and acetone.

*Source: U.S. EPA, 1975; Reidies, 1981

3.1.1.2.5. Manganous Oxide -- MnO is found in nature as manganosite and is manufactured by reducing higher oxides with carbon monoxide or coke or by thermal decomposition of manganous carbonate. It is a good starting material for preparing other manganous salts and has some use in ferrites, in welding, and as a nutrient in agricultural fertilizers.

3.1.1.2.6. Manganous Phosphate -- $Mn_3(PO_4)_2$ is made from carbonate and phosphoric acid. It is used as an ingredient of proprietary solutions for phosphating iron and steel.

3.1.1.2.7. Manganous Sulfate -- $MnSO_4 \cdot H_2O$ can be made by treating any manganese compound with sulfuric acid. It is also a co-product in the manufacture of hydroquinone. In pure state it is used as a reagent. Its major use is as a nutrient in fertilizers and in animal feeds.

3.1.1.2.8. Manganese Soaps -- Manganese(II) salts of fatty acids (2-ethyl hexoate, linoleate, naphthenate, oleate, resinate, stearate, and tallate) are used as catalysts for the oxidation and polymerization of oils and as paint driers.

3.1.1.1.9. Other Manganese (II) Compounds -- Other commercially available Mn(II) compounds include the acetate, borate, chromate, fluoride, formate, gluconate, glycerophosphate, hydroxide or "hydrate", hypophosphite, nitrate, nitrite, perchlorate, sulfide, and sulfite.

3.1.1.3. MANGANESE (IV) COMPOUNDS --

3.1.1.3.1. Manganese Dioxide -- MnO_2 is the most important Mn(IV) compound and the most important commercial compound of manganese. In nature it occurs as pyrolusite, the principal ore of manganese, as well as in several other less common minerals. More than 90% of manganese dioxide is used in the production of ferromanganese and other alloys and of manganese metal. The rest is used for the production of dry cell batteries and chemicals, and as an oxidant in the manufacture of some dyes.

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Manganese dioxide is insoluble in water. This property confers stability, since the ion Mn^{4+} is unstable in solution. On heating, it forms other oxides, Mn_2O_3, Mn_3O_4 and MnO. Hydrated forms are obtained by reduction of permanganates in basic solution. In acid solution it is an oxidizing agent. The classic example is the oxidation of HCl which has been a convenient means of chlorine generation both in the laboratory and in the Weldon process for manufacturing chlorine commercially (Hay, 1967).

$$MnO_2 + 4HCl \rightarrow Mn^{4+}Cl_4 + 2H_2O$$

$$Mn^{4+}Cl_4 \rightarrow Mn^{3+}Cl_3 + 1/2Cl_2$$

$$\overset{warm}{Mn^{3+}Cl_3 \rightarrow Mn^{2+}Cl_2 + 1/2Cl_2}$$
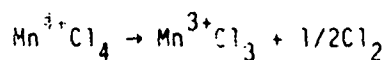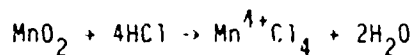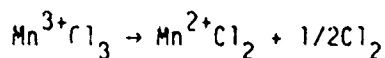
Manganous sulfate and oxygen are produced in hot sulfuric acid in the presence of a little MnO as catalyst. Hydrogen fluoride reacts with manganese dioxide at 400-500°C to produce manganous fluoride and oxygen (Hay, 1967).

Manganese dioxide can react with sulfur dioxide in two ways:

1. $$MnO_2 + SO_2 \rightarrow MnSO_4$$

2. Alternatively, it can occur stepwise:

$$2MnO_2 + 3SO_2 \rightarrow Mn_2(SO_3)_3 + 1/2O_2$$
$$Mn_2(SO_3)_3 \rightarrow MnS_2O_6 + MnSO_3$$
$$MnSO_3 + 1/2O_2 \rightarrow MnSO_4$$
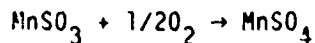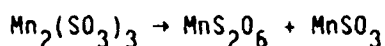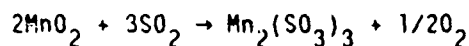
The end products of this series of reactions are MnS_2O_6 (manganese dithionate) and $MnSO_4$ (Hay, 1967). Nitrogen dioxide also reacts similarly with MnO_2 to form manganous nitrate, $Mn(NO_3)_2$ (Sullivan, 1969).

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3.1.1.4.   MANGANESE (VII) COMPOUNDS --

3.1.1.4.1.   Potassium Permanganate -- $KMnO_4$ is an important indus-
trial chemical as well as an analytical reagent (Reidies, 1981). Its use is
based on its oxidizing ability. It is used in the organic chemical indus-
try, in the alkaline pickling process, and in cleaning preparatory for
plating. It is also used for water purification and odor abatement in
various industrial wastes. Other permangarates, although less important,
are also available commercially.

Manganese (VII) permanganates (almost always potassium permanganate) are
used in a host of oxidations including reactions with both inorganic and
organic compounds (Hay, 1967). In moderately alkaline solution, the oxidiz-
ing reaction is:

$$2KMnO_4 + H_2O \rightarrow 2KOH + 2MnO_2 + 3(0)$$

In neutral solution,

$$2KMnO_4 + MgSO_4 \text{ (buffer)} + H_2O \rightarrow K_2SO_4 + Mg(OH)_2 + 2MnO_2 + 3(0)$$
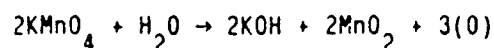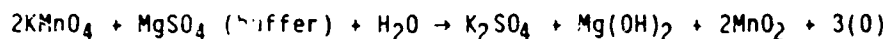
while in acid solution it reacts as

$$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5(0)$$
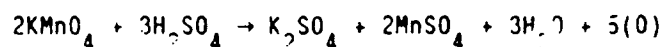
In organic reactions $(MnO_4)^-$ is a most versatile oxidant, the activ-
ity of which can be controlled to a great extent not only by the molecular
nature of the compound undergoing oxidation but also by the acidity or
alkalinity and other reaction conditions. It is potentially a more vigorous
oxidant than dichromate.

3.2.   SAMPLING AND ANALYTICAL METHODS

Determination procedures consist of three main steps: sampling, sample
preparation and analysis. In trace metal determination, sample preparation
often also includes a preconcentration or a preseparation step.

3.2.1. Sampling.

3.2.1.1. AIR -- Virtually all of manganese present in air is inorganic, in the form of suspended particulate matter, and is collected by sampling procedures for airborne particulates. Organic manganese compounds in the gas phase are not normally present in air in detectable concentrations (see Section 3.5.2.1.), although sampling and analysis techniques have been described (Ethyl Corporation, 1972; Coe et al., 1980). Therefore, description of air sampling procedures will be limited to methods designed for particulates.

3.2.1.1.1. In-plant Air -- In the past, the impinger was widely used for the sampling of particulate air contaminants (ACGIH, 1958). However, owing to a low efficiency for particles smaller than 1 μm in diameter (Davies et al., 1951) and impractical handling and transportation, the impinger has been replaced by filtering media: 1) glass fiber filters, which have a low resistance to air flow, have high efficiency for submicron particles, and are hydrophobic so that they can be weighed without trouble; and 2) organic membrane filters, which are soluble in organic solvents and strong acids. Electrostatic precipitators have also been used in the working environment. They have a high collection efficiency for particles of all sizes, but are less practical and versatile in field use than filters, and cannot be used in potentially explosive atmospheres.

3.2.1.1.2. Ambient Air -- High-volume (HI-VOL) samplers are frequently used to collect samples of airborne particles from ambient air for trace metal analysis. These samplers typically use glass fiber filters, 20x25 cm, and collect particles from about 2500 m^3 of air in 24 hours. Several hundred samplers of this type are currently in use as part of the National Air Surveillance Networks (NASN), and thousands are in use by state and

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local agencies (Thompson, 1979; U.S. EPA, 1979a). Prior to 1977, filters from the NASN were composited for analysis on a quarterly basis, but since then improved analytical efficiency has enabled analysis of individual filters (U.S. EPA, 1979a).

High-volume samplers with organic membrane filters of 10 cm diameter, sampling 200 m^3 of air over 24 hours, and low-volume samplers with membrane filters of 2.5 cm diameter, sampling 25-30 m^3 over a week, have also been used (WHO, 1976; Saric, 1978). Manganese can be conveniently determined on both membranous and fibrous filters (Fugas, 1980); however, fibrous filters should not be used when the method of analysis is x-ray fluorescence (U.S. EPA, 1981c).

Particle size is an important factor in determining human exposure to an ambient aerosol (see Section 3.6.4.1.). High-volume samplers may sample particles as large as 50-100 μm in diameter (Bernstein et al., 1976; Thompson, 1979) and thus do not provide any specific information on particle size. A variety of samplers achieving some degree of particle size discrimination have been used for ambient trace metal analyses, including cascade impactors (Lee et al., 1972) and cyclones (Bernstein et al., 1976; Bernstein and Rahn, 1979). However, dichotomous samplers are now most widely used for this purpose. Samplers of this type separate fine and coarse particles by use of a virtual impactor (Dzubay and Stevens, 1975). The fine particle cut-off (D_{50}), at which 50% of larger-diameter particles are excluded, ranges from 2-3.5 μm depending on the sampler used. A fractioning inlet also is often used to determine the upper size limit for the coarse fraction; D_{50} is normally set at 10, 15 or 20 μm (e.g., U.S. EPA, 1981a). Particles for metal analysis are typically collected on a teflon or cellulose filter of ~1 μm pore size and ~6-25 cm^2 surface area

(e.g., Lewis and Macias, 1980; Ozubay et al., 1982). Flow rates vary from 14-50 ℓ/min, and sampling times from 2-24 hours (e.g., Stevens et al., 1978).

3.2.1.1.3. Stationary Source Emissions -- Glass fiber filters are used for sampling manganese particles in stacks, often in the form of a filter thimble to increase the sampling surface and thus reduce air flow resistance. For low temperature flue gases ($=100^{\circ}C$), membrane or cellulose filters may be used as well. Sampling is usually performed iso-kinetically, and the filter holder is placed in the stack or heated during sampling to prevent condensation. In the classical sampling train for the collection of particles (36 FR 24876; U.S. EPA, 1978a), the filter holder is followed by a series of impingers for the collection of condensate in order to measure moisture content and to protect the pump and the gas meter. Impingers can be replaced by a condensor. Cascade impactors are available for collecting samples of particles by size from the stack (Pilat et al., 1970) and are sometimes preceded by a cyclone to prevent the massing of large particles on the first separation stage (Instrumentation for Environmental Monitoring, 1975).

3.2.1.1.4. Mobile Source Emissions -- Standard tests of motor vehicle emissions measure only gaseous pollutants (CO, NO_x and hydrocarbons), but for   ·ty vehicle·   :asurements using optical methods are also used (37 FR 24250).   .. or the filters in the sampling system is to remove particles from the ·'s stream. The composition, m   · lead content and particle size,   only under experimental conditio   , · samples, collected in lar·   ..e federal emission

test cycle, were diluted 8 to 1 with dry air in order to prevent condensation, and a known volume of the mixture was sampled through a membrane filter.

For particle size analysis, either microscopic counting of electrostatic precipitator samples (Hirschler and Gilbert, 1964) or size selective sampling by cascade impactor was used (Mueller et al., 1963). The samples were collected from a tailpipe by a probe (Ter Haar et al., 1972) or else a mixing tunnel was used for proportional sampling (Habibi, 1970).

3.2.1.2. WATER -- The sampling of water and wastewater can be by grab or composite sample (minimal portions 25 mℓ). Samples are collected in bottles of glass or plastic (U.S. EPA, 1973; King, 1971). Preparation of bottles to prevent contamination is discussed by Moody and Lindstrom (1977), and possible wall losses by Bond and Kelly (1977).

3.2.1.3. FOOD -- According to the sampling objective, samples of food consist of cooked, raw, or packed food. Piscator and Vouk (1979) described three methods currently available for estimating intake of metals via food products:

1. To collect and analyze samples of single foodstuffs for the metal, and then estimate the ingested amount of metal.

2. To collect and analyze certain classes of food in the amounts that are actually consumed and make estimates from that.

3. To collect and analyze duplicate samples of the meals people have eaten during a certain period.

The first of the three methods is recommended by the Food and Agricultural Organization/World Health Organization (FAO/WHO, 1977); the second method has been used by the U.S. FDA (1978).

3 2.1.4. SOIL -- Samples of soil are collected either area wide or along a transect. The variability in the soil complex makes it desirable to take paired samples.

Profile samples are collected either by digging a hole at a sample site and taking an undisturbed slice from the side of the hole, or layer by layer to t depth desired. The samples are screened to remove organic matter, stones, and lumps, and are thoroughly mixed. A more detailed description can be found in Bear (1964).

3.2.1.5. BIOLOGICAL MATERIALS --

3.2.1.5.1. Urine -- Samples of urine are collected either in glass (Ajemian and Whitman, 1969) or polyethylene bottles (Stoeppler et al., 1979) with the addition of redistilled HCl at pH 2, and are kept under refrigeration before analysis. Preferably, 24-hour samples should be collected (Tichy et al., 1971).

3.2.1.5.2. Blood -- Samples of blood are obtained by venipuncture and transferred to polyethylene tubes. If serum is used for further analysis, blood is allowed to clot and serum is separated by centrifugation (D'Amico and Klawans, 1976). If whole blood is analyzed, heparin is added (Tsalev et al., 1977). This, however, can introduce contamination according to Bethard et al. (1964), who used citrate dextrose as a coagulant. Additional possible sources of contamination are discussed by Cotzias et al. (1966).

3.2.1.5.3. Tissue and Organs -- Tissue or organ samples should be dissected with knives in a dust-free atmosphere, placed in a polyolefin vessel, and stored deep frozen until analysis (Stoeppler et al., 1979).

3.2.1.5.4. Hair and Other Biological Samples -- Samples of hair are cut close to the scalp (Gibson and DeWolfe, 1979) and stored in polyethylene bags.

Samples of nails (Hopps, 1977), teeth (Langmyhr et al., 1975), skin (Parkinson et al., 1979), and sweat (Hopps, 1977) have also been used for manganese analysis.

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3.2.2. Sample Preparation. While sampling is rather specific for various environmental media, the procedures for sample preparation and analysis are often the same. Unless a nondestructive method is used for analysis, samples have to be transformed first into solution by dry, wet, or low temperature ashing and acid digestion. The conventional ashing in a muffle furnace results in loss of a number of trace elements (Thompson et al., 1970), but manganese can be treated by any ashing procedure without an appreciable loss. After digestion of the samples with nitric acid, the acid has to be expelled, and manganese in the residue is dissolved in hydrochloric acid.

Glass fiber filters are not destroyed in the ashing procedure; therefore, it is better to remove manganese by acid extraction (Thompson et al., 1970) in order to avoid filtration which is a source of wall losses in trace metal analysis (Hrsak and Fugas, 1980). Extraction, with a mixture of nitric and hydrochloric acids, may be carried out by refluxing after ashing of the sample (U.S. EPA, 1979a), or by sonification in the acids at $100°C$, without ashing. The latter method is currently used by the U.S. EPA (1983a).

If small concentrations of manganese are present in a large volume of sample (e.g., water or urine), it may become necessary to increase the concentration of manganese to a measurable level by reducing the volume of the solution by evaporation. To avoid contamination, nonboiling evaporation in Teflon tubes (Boutron and Martin, 1979) or "vapor filtration" through a vapor-permeable membrane (U.S. EPA, 1978b) have been used. A simultaneous increase in the concentration of other substances present in the sample in much higher concentrations may cause turbidity, coprecipitaton, or other type of interference caused by the "matrix effect." In such cases a pre-separation step is indicated. It is usually based on chelation, either

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selective, e.g., with thinoyltrifluoroacetone (Saric, 1973) or nonselective, as with 8-hydroxyquinoline (Ajemian and Whitman, 1962; Klinkhammer, 1980; Vanderborgnt and Van Grieken, 1977) and cupferron (Van Ormer and Purdy, 1973; Buchet et al., 1976) or by ion exchange on Chelex 100 (Lee et al., 1977) or Dovex A1 (Riley and Taylor, 1968). Coprecipitation with diethyl dithiocarbamate (Watanabe et al., 1372) or dibenzyldithi. arbamate (Li et al., 1978) also has been applied for enrichment of samples as has electrodeposition (Wundt et al., 1979). Radio-chemical separation is most often used before the analysis of irradiated samples (Cotzias et al., 1966; Hahn et al., 1968; Versieck et al., 1973).

Samples of plants, raw food, or hair have to he cleaned before further treatment. Care should be taken not to contaminate the sample during this operation. Detergents or solvents have been used for washing hair samples. However, while surface contamination is being removed, weakly bound metals also may be removed from hair. Hair washing procedures are discussed by Chittleborough (1980).

3.2.3. Analysis. The selection of available analytical methods for the determination of manganese has increased in recent years, and methods of preference have changed.

Some 30 years ago colorimetric (Standard Methods for the Examination of Water and Wastewater, 1971) or spectrographic (Thompson et al., 1970) methods were used the most. Polarographic methods had a number of supporters but never became very popular. Polarographic and voltametric analyses are now regaining some popularity since new techniques have been developed with a high resolution and sensitivity, such as the pulsed stripping technique (Flato, 1972). Colorimetric methods are still used, especially in water analysis, and are now coupled with an autoanalyzer (Crowther, 1978).

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The introduction of atomic absorption spectrophotometry (AAS) in 1955 proved to be a turning point in analytical practice. Although many other new and sophisticated methods have been developed, none has experienced such a wide acceptance as AAS. The introduction of Delves cups (Delves, 1970), and flameless techniques using the carbon rod (Matousek and Stevens, 1971) and graphite furnace (Slavin et al., 1972), made it possible to analyze microliter samples with little or no pretreatment, although with less precision and at a higher cost.

DC arc optical emission spectrometry (OES) was used by U.S. EPA until 1976 for multi-elemental analysis of NASN high-volume samples collected on glass fiber filters (U.S. EPA, 1979a). The method currently used for this purpose is inductively coupled argon plasma optical emission spectrometry (ICAP) (U.S. EPA, 1983b). Since instrumental detection limits are lower than most blank filter analyses, the limits of discrimination are determined mainly by filter characteristics. The limit of discrimination for manganese on filters used by the NASN in 1975-1976 was ~0.0025 $\mu g/m^3$ (U.S. EPA, 1979a).

X-ray fluorescence (XRF) is also used in multi-element analysis (Gilfrich et al., 1973). Problems include particle size effect (Davison et al., 1974), self absorption (Dzubay and Nelson, 1975), and the preparation of standards with a matrix matching that of the sample. This method is not used with fibrous filters, but is the most popular for use with membrane filters, as are commonly used with dichotomous samplers. Detection limits of ~20 ng/cm^2 of filter surface area have been indicated for manganese. For a 24-hour sampling period with typical filters and flow rates, detection limits of 0.002-0.007 $\mu g/m^3$ in air are obtained (Dzubay and Stevens, 1975; Stevens et al., 1978).

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Neutron activation analysis (NAA) has been used for the determination of manganese in various environmental media, mostly in multi-element analysis (Robertson and Carpenter, 1974). NAA suffers from interferences such as the production of the same radioisotope by another element or one with a close radiation peak, but most of these can be eliminated by optimizing irriuation, decay, and counting times. The method is sensitive, but more costly and less frequently available than XRF (U.S. EPA, 1981c).

Both NAA and XRF are basically nondestructive methods of analysis, but if a greater sensitivity is required, a separation and preconcentration step cannot be avoided for aqueous samples (Lee et al., 1977; Buono et al., 1975; Watanabe et al., 1972; Linder et al., 1978).

Instrumental detection limits for manganese by several analytical techniques are shown in Table 3-4. Reported sensitivities for any method vary depending on the type of instrument, the preparation or enrichment of the sample, and on the way of expressing the result. It is difficult to compare the sensitivities claimed by researchers using various methods since the result may be expressed as absolute amount, concentration per mℓ of final solution, or per unit of measure of the medium from which the sample was taken.

3.3. PRODUCTION AND USE

3.3.1. Production. The ferroalloy industry uses manganese-bearing ore to produce several manganese alloys and manganese metal. Production may be carried out using a blast furnace, an electric arc furnace or electrolytically (Bacon, 1967; U.S. EPA, 1974; Matricardi and Downing, 1981).

TABLE 3-4

Relative Sensitivity of Some Important
Analytical Techniques for Manganese*

Analytical Method	Detection Limit (ng)
Neutron activation analysis	0.005
Optical emission spectroscopy (DC arc)	10
Atomic absorption spectrophotometry	0.5
Spark source mass spectrometry	0.05

*Source: U.S. EPA, 1975

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For blast furnace production of ferromanganese (an alloy of manganese and iron) the furnace is charged with a blend of ores, coke and limestone, or dolomite, and operated at low blast pressures. The composition of the charge is carefully controlled to decrease the slag production, minimize dust losses, and allow uniform gas distribution throughout the furnace. This is done by careful choice of the chemical composition of the charge as well as the size distribution. High manganese recovery is favored by: 1) small slag volume, 2) a basic slag, 3) high blast temperatures, and 4) coarse ores. The limit of capacity is determined by the loss of manganese by volatilization. Blast furnace production of ferromanganese was last used in this country in 1977; production is now primarily by electric submerged-arc furnace.

In submerged-arc furnace production, the charge, consisting of manganese ore, coke and dolomite, is placed in the furnace by continuous or intermittent feed. Vertically suspended carbon electrodes extend down into the charge, and carbon reduction of the metallic oxides takes place around the electrodes. Carbon monoxide gas is produced in large quantities, and rises from the charge carrying entrained fume particles. Submerged-arc furnaces may have open tops, may be partially sealed (mix-sealed), or completely sealed. The open furnaces vent larger quantities of gas due to mixing of air with the process gases

Silicomanganese is an alloy of manganese and iron, also produced by smelting of ore in an electric submerged-arc furnace. It differs from standard ferromanganese in that the furnace charge contains large amounts of quartz, and the resulting alloy . lower in carbon and higher in silicon.

For electrolytic production of high-purity manganese metal, the ore is leached with sulfuric acid at pH 3 to form manganese sulfate. The solution

is adjusted to pH 6 by the addition of ammonia or calcined ore to preci-pitate the iron and aluminum. Arsenic, copper, zinc, lead, cobalt and molybdenum are removed as sulfides after the introduction of hydrogen sul-fide gas. Ferrous sulfide and air is added to remove colloidal sulfur, colloidal metal sulfides, and organic matter. The purified liquid is then electrolyzed.

Manganese metal can also be produced via a fused-salt electrolysis pro-cess. The process is similar to the Hall method of producing aluminum. The manganese ore is reduced to the manganese(II) level and charged to an elec-trolytic cell containing molten calcium fluoride and lime. The manganese is formed in a molten state.

A number of compounds of managanese also are commercially produced. Manganese oxide (MnO) is produced by reductive roasting of ores high in managanese dioxide (MnO_2). MnO is an important precursor of several other commercially-produced compounds, including electrolytic manganese dioxide, a high-purity product formed by electrolysis of MnO. Potassium permanganate is produced by a liquid-phase oxidation of managanese dioxide ore with potassium hydroxide, followed by electrolysis (Reidies, 1981). United States production capacities for several compounds are shown in Table 3-5.

Manganese supply-demand relationships for the years 1969-1979 are given in Table 3-6 A small proportion of the manganese smelted in this country is mined domestically, the bulk is imported. However, ore imports have declined recently since imports of alloy and metal have increased and over-all demand for ferroalloys has decreased somewhat. Domestic production of ferromanganese has declined steadily since 1965; silicomanganese production has also declined recently (Table 3-7).

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TABLE 3-5

Estimated United States Production, Capacity
and Use of Selected Manganese Compounds*

Product	Formula	Estimated U.S. Production Capacity (mt/yr)	Use
Electrolytic manganese dioxide	MnO_2	18,000	Dry-cell batteries; ferrites
High purity manganese oxide	MnO	9,000	High-quality ferrites; ceramics; intermediate for high purity Mn(II) salts
60% manganese oxide	MnO	36,000	Fertilizer; feed additive, intermediate for electrolytic manganese metal and dioxide
Manganese sulfate	$MnSO_4$	68,000	Feed additive; fertilizer; intermediate for many products
Manganese chloride	$MnCl_2$	3,000	Metallurgy; MMT synthesis; brick colorant; dye; dry-cell batteries
Potassium permanganate	$KMnO_4$	14,000	Oxidant; catalyst; intermediate; water and air purifier
Methylcyclopentadienyl manganese tricarbonyl (MMT)	$CH_3C_5H_4Mn(CO)_3$	500-1,000	Fuel additive

*Source: Adapted from Reidies, 1981

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TABLE 3-6

Manganese Supply-Demand Relationships, 1969-1979[a]
(thousand short tons, manganese content)

	1969	1970	1971	1972	1973	1974	1975	1976	1977	1978	1979
World Production											
Mine production:											
United States	93	66	38	29	31	35	19	31	27	38	31
Rest of world	9,192	6,978	9,960	9,983	10,707	10,185	10,791	11,007	9,547	9,544	10,487[b]
Total	9,285	9,044	9,998	10,012	10,738	10,220	10,810	11,038	9,574	9,582	10,518[b]
Components and Distribution of U.S. Supply											
Domestic mines	93	66	38	29	31	35	19	31	27	38	31
Shipment of Government stockpile excess	50	140	118	218	242	807	309	294	358	279	264
Imports, ore	992	847	938	793	722	593	766	649	454	278	244
Imports, alloy and metal	257	238	212	305	336	376	346	478	481	604	708
Industry stocks, Jan. 1	1,180	1,241	1,175	1,261	1,241	978	1,183	1,359	1,373	1,092	811
Total U.S. supply	2,572	2,532	2,481	2,626	2,572	2,789	2,623	2,811	2,693	2,291	2,058
Distribution of U.S. supply:											
Industry stocks, Dec. 31	1,241	1,175	1,281	1,241	978	1,183	1,359	1,373	1,092	811	749
Exports, ore	10	10	25	12	29	107	125	64	69	100	29
Exports, alloy and metal	4	20	5	7	11	7	6	10	9	17	30
Demand	1,317	1,327	1,170	1,366	1,554	1,492	1,133	1,364	1,523	1,363	1,250
U.S. Demand Pattern											
Construction	268	260	252	236	325	317	249	238	240	279	291
Transportation	253	226	261	239	340	315	260	298	300	317	296
Machinery	185	176	175	171	229	245	185	186	188	216	217
Cans and containers	62	73	71	58	72	79	59	63	60	60	61
Appliances and equipment	51	51	51	51	68	68	47	51	53	59	59
Oil and gas industries	43	42	46	44	63	69	64	53	63	74	70
Chemicals	37	37	35	50	54	65	52	47	61	61	59
Batteries	20	20	19	18	18	18	16	18	18	18	17
Other[c]	398	442	260	499	385	316	201	410	540	280	180
Total U.S. primary demand	1,317	1,327	1,170	1,366	1,554	1,492	1,133	1,364	1,523	1,363	1,250

[a] Source: DeHuff and Jones, 1980

[b] Estimated

[c] Includes processing losses

TABLE 3-7

Net United States Production
of Ferromanganese and Silicomanganese[a]

Year	Ferromanganese (10^3 short tons)	Silicomanganese (10^3 short tons)
1982	(120)[b]	(75)[b]
1981	193	173
1980	189	188
1979	317	155
1978	273	142
1977	334	120
1976	483	129
1975	576	143
1974	544	196
1973	683	184
1972	801	153
1971	760	165
1970	835	193
1969	852	223
1968	880	284
1967	941	246
1966	946	253
1965	1148	--
1964	929	203
1963	751	152
1962	781	136
1961	733	120
1960	843	101

[a]Source: U.S. Bureau of Mines (Jones, 1982; DeHuff and Jones, 1981; DeHuff, 1961-1980)

[b]Estimated gross production; exceeds net production (U.S. Bureau of Mines, 1983)

3.3.2. Use. The principal use of manganese is in metallurgy, which accounts for ≈95% of United States demand for all forms of manganese (Reidies, 1981) and ≈99% of manganese alloys and metal (DeHuff and Jones, 1981). The majority (>90%) of metallurgical use is in steel production, for which manganese is indispensible (Matricardi and Downing, 1981; Bacon, 1967). Its function is 3-fold: 1) it combines with sulfur, eliminating the principal cause of hot-shortness; 2) it acts as a deoxidizer or cleanser in molten steel; 3) in certain steels it is used as an alloying element to improve the strength, toughness, and heat-treating characteristics of structural and engineering steels.

Several different manganese alloys, as well as high-purity manganese metal, are used to introduce manganese into steels, pig iron, and some non-ferrous alloys (Bacon, 1967). The various forms are listed in Table 3-8, along with their composition and use.

A minor use of manganese metal, in various powdered forms, is in military and civilian pyrotechnics and fireworks. It is used to produce extremely bright flares and lighting devices. Annual consumption for this application may be on the order of several hundred tons per year.

A variety of compounds of manganese are used in the chemical industry and battery manufacture; these uses accounted for 4.7 and 1.4% of total United States manganese demand in 1979 (see Table 3-6). Some major uses are as follows: feed additives and fertilizers (MnO, $MnSO_4$), colorants in brick and tile manufacture (various oxides, $MnCl_2$), dry cell battery manufacture (electrolytic MnO_2, $MnCl_2$), chemical manufacture and processing ($KMnO_4$, $MnCO_3$, $MnCl_2$) and fuel additives (MMT) (see Table 3-5).

MMT was introduced in 1958 as an antiknock fuel additive (U.S Dept, 1962). This compound has been used at a concentration of 0.025 g Mn/gal in

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TABLE 3-8

Commercial Forms of Manganese[a]

Name	Composition[b]	Use
High purity manganese	99.5% manganese 0.15% (max) hydrogen 0.030% (max) sulfur 0.005% (max) iron 0.005% (max) carbon 0.001% (max) phosphorus, aluminum, silicon	ferrous metals: free-machining steels flat-rolled low-carbon steels Non-ferrous metals (improves strength, ductility and hot-rolling properties) aluminum alloys aluminum-bronze constantan monel everdur nickel-chromium nickel-silver manganese-bronze for ship propellers
Low-carbon ferromanganese	95-90% manganese 2.0% (max) silicon 0.07-0.75% carbon 0.2% (max) phosphorus 0.02% (max) sulfur	Stainless steels where low carbon content is essential
Medium-carbon ferromanganese·	80-85% manganese 1.25-1.50% carbon 1.0% (max) silicon 0.3% (max) phosphorus 0.02% (max) sulfur	For use in steels with carbon specifications too low to permit use of standard ferromanganese
Standard ferromanganese	78-82% manganese up to 7.5% carbon 1.2% (max) silicon 0.35% (max) phosphorus 0.05% (max) sulfur	Used in production of Bessemer, open-hearth and electric furnace steels for forging, rolled products, and castings
Low-iron ferromanganese	85-90% manganese 7% carbon 3% silicon 2% iron	·Used in making alloys with non-ferrous metals such as aluminum, nickel, and copper.
Spiegeleisen	16-19% manganese 6.5% carbon 1.0-3.0% silicon 0.08% (max) phosphorus 0.05% (max) sulfur	A white cast iron with low phosphorus and sulfur, used for making alloy additions and as a cleaning agent.

TABLE 3-8 (cont.)

Name	Composition[b]	Use
"MS" ferromanganese	80-85% manganese 1.25-1.50% carbon 0.35% silicon	Used for making screw-stock where high silicon content destroys machining properties.
"DQ" ferromanganese	86% manganese 0.45% carbon 0.40% silicon 0.17% phosphorus	Used as a manganese additive to steels for drawing quality steel sheets.
Exothermic ferromanganese	--	Briquets when added to steel cause an exothermic reaction--used for ladle additions of manganese to prevent chilling.
Ferromanganese-silicon	63-66% manganese 28-30% silicon 0.08% (max) carbon 0.05% (max) phosphorus	For partial slag reduction and manganese additions in the production of the 300 series of stainless steels, for large manganese additions to the 200 series of stainless steels, and in nongrain-oriented silicon electric steels and low-carbon, low-alloy steels as a ladle addition of manganese and silicon.
Silicomanganese	65-68% manganese 18.5-21% silicone 1.50% carbon 0.2% (max) phosphorus 0.04% (max) sulfur	Used in open-hearth steelmaking practice as a blocking agent (i.e., to prevent the reaction between carbon and oxygen) for engineering steels with carbon content of 0.10-0.15%.
Calcium-manganese-silicone	53-59% silicon 16-20% calcium 14-18% manganese	In high quality steel castings to improve tensil strength, elongation, and impact strength.
Manganese-aluminum master alloys	75% manganese 25% aluminum	Used in aluminum alloys to impart strength, hardness, and stiffness.

[a]Source: Bacon, 1967 and DeHuff, 1975

[b]Composition is given for Grade A product; other grades will have the same impurities, but in a higher percentage. The balance of each composition necessary to make 100% is mainly iron.

fuel oil and 0.08-0.5 g Mn/gal in turbine fuels, and has been used to a small extent in leaded gasoline (Ter Haar et al., 1975). Production prior to 1974 was ≈500 tons/year (≈125 tons Mn/year) (Piver, 1974). Beginning in 1974, MMT was used in unleaded gasoline at concentrations up to 0.125 g Mn/gal; use in the 12 months prior to its ban in September, 1978 was reported by Ethyl Corporation as ~3750 tons/year (~940 tons Mn/year) (Hall, 1983b). Some adverse effects of MMT on catalytic converter performance and hydrocarbon emissions were reported (U.S. EPA, 1977b), and MMT use in unleaded gasoline was banned in October, 1978. The ban continues in effect, except that MMT use at 0.031 g Mn/gal was permitted during a 4-month period in 1979, due to a shortage of unleaded fuel (44 FR 32281-32282). MMT continues to be used in ≈20% of leaded gasoline at levels of ≈0.05 g Mn/gal, and is used in Canada in the majority of unleaded gasolines at levels of up to 0.068 g Mn/gal (Hall, 1983a). Options for its future use at low levels in United States unleaded gasoline continue to be studied (Hall, 1983a).

3.4. SOURCES OF MANGANESE IN THE ENVIRONMENT

3.4.1. Crustal Materials and Soils.

Manganese is widely distributed in the earth's crust. It is considered to be the 12th most abundant element and fifth most abundant metal. Manganese is exceeded in abundance by aluminum, iron, magnesium and titanium; it is more abundant than nickel, copper, uranium, zinc, lead and vanadium. The concentration of manganese in various components of the earth's crust ranges from near zero to 7000 μg/g. A rough estimate of the average concentration of manganese in the earth's crust is about 1000 mg/kg (DeHuff, 1973). Tureklan and Wedepohl (1961)

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suggested the following distribution of manganese, expressed in µg/g, for the major units of the earth's crust:

1. Igneous rock: ultrabasic, 1620; basaltic, 1500; high-calcium granitic, 540; low-calcium granitic, 390; and syenitic, 850

2. Sedimentary rock: shales, 850; sandstones, essentially zero; and carbonates, 1000

3. Deep-sea sediment: carbonate, 1000; and clay, 6700

Hodgson (1963) reported concentrations of manganese in µg/g for various types of rocks and for soil: 1000 in earth's crust; 2000 in basic rocks; 600 in acid rocks; 670 in sedimentary rocks; 850 in soils.

Manganese is a major constituent of at least 100 minerals and an accessory element in more than 200 others (Hewett, 1932). Manganese-containing minerals include anhydrous and hydrous oxides, carbonates, anhydrous and hydrous silicates, sulfides, anhydrous and hydrous phosphates, arsenates, tungstates, and borates. The most common manganese minerals and the percentages of manganese contained therein are listed in Table 3-9.

Relatively little manganese is mined within the United States (Sittig, 1976). Manganese deposits are well-distributed through the southern Appalachian and Piedmont regions, the Batesville district of Arkansas and many of the western states. These deposits have been exhausted in terms of mining for profit at existing or appreciably higher prices. There are large low-grade manganese deposits extending for miles along both sides of the Missouri River in South Dakota and large low-grade deposits in the Cuyuna Range of Minnesota, in the Artillery Mountains region of northwestern Arizona, in the Batesville district of Arkansas, in Aroostok County in Maine, and to a lesser extent in the Gaffney-Kings Mountain district of North Carolina and South Carolina. Manganese ore ($\geq 35\%$ Mn) is no longer mined in the United States, but some manganiferous ore (5-35% Mn) is mined in Minnesota, New Mexico and South Carolina (DeHuff and Jones, 1980)

TABLE 3-9

Manganese Content of Selected Minerals*

Mineral	Formula	Manganese Content (%)
Pyrolusite	MnO_2	60-63
Manganite	$MnO(OH)$	62
Hausmannite	Mn_3O_4	72
Rodochrosite	$MnCO_3$	47
Rhodonite	$MnSiO_3$	42
Braunite	$3Mn_2O_3, MnSiO_3$	63
Pyrochroite	$Mn(OH)_2$	61
Alabandite	MnS	63

*Source: Hewett, 1932

Researchers report various concentrations of manganese in different types of soils. Swaine (1955) reported a range of 200-3000 µg/g for total content of manganese in most soils. Wright et al. (1955) studied virgin profiles of four Canadian soil groups and reported a manganese content of 250-1380 µg/g. Swaine and Mitchell (1960) studied representative Scottish soil and reported a range for total manganese of 50-7000 µg/g in air-dried soil. Shacklette et al. (1971) analyzed various soil samples in the United States and reported a range of manganese content from <1-7000 µg/g, with an arithmetic mean of 560 µg/g.

Crustal materials are entrained into the atmosphere by a number of natural and anthropogenic processes, and thus compose an important fraction of atmospheric particulate. These processes include vehicle suspension of road dusts, wind erosion and suspension of soils (especially through agriculture or construction activities), and quarrying processes (Dzubay et al., 1981). The resulting, mechanically-generated aerosols consist primarily of coarse particles (>2.5 µm) (Dzubay, 1980). Since manganese is a typical constituent of these dusts, some researchers have used this element as a tracer to determine the degree of contributions from these sources in ambient aerosol (Kleinman et al., 1980; Kneip et al., 1983).

Several other processes also result in the ejection of crustal materials to the atmosphere; for example, the smelting of natural ores and the combustion of fossil fuels. However, these differ from the above categories in that much of the material is released in the form of fume or ash in the fine particle range (<2.5 µm). In addition, these tend to be point sources subject to control measures, whereas the above typically are not. These industrial and combustion processes will be discussed in Section 3.4.2. The relative contributions of all sources to fine and coarse particulate in ambient air will then be discussed in Section 3.4.3.

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3.4.2. Industrial and Combustion Processes. Manganese is released to the atmosphere during the manufacture of ferroalloys, iron and steel, other alloys, batteries, and chemical products. Combustion of fossil fuels also results in release. Emissions from these sources in 1968 were estimated by the U.S. ⸺ ⸺ (1971), as shown in Table 3-10. This national inventory

⸺ that nearly half of all industrial and combustive emissions of ⸺ ⸺ were from ferroalloy manufacture, over one-third were from iron and steel manufacture, about one-tenth were from fossil fuel combustion, and minor amounts (<1%) were generated by other processes. Since 1968, pro-esses, control measures, and production volumes have changed substantially in many categories. Thus the emissions estimates in Table 3-10 will be used ⸺ as a basis for discussion; more recent emissions estimates are not available. The most important sources are discussed in the following sections.

3.4.2.1. FERROALLOY MANUFACTURE -- The manufacture of manganese alloys and metal has been the major source of manganese emissions to the atmosphere (see Table 3-10), and has been responsible for the highest recorded ambient manganese concentrations (see Section 3.6.1.2.). Dust varying from 3-100 μm in size is emitted from crushing, screening, drying and mixing of both raw materials (~0.3% loss) and product (~0.5% loss), but the majority of pollution is from the furnace (U.S. EPA, 1981b). Furnace particulate emissions contain 15-25% manganese, primarily in the form of oxides. Silicates are a second major constituent. Particle size is predominantly fine (<2 μm).

Total U.S. emissions of manganese from ferroalloy manufacture were estimated at ~8400 mt in 1965 (see Table 3-10) but current emissions are probably much lower. Production of ferromanganese and silicomanganese, the

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